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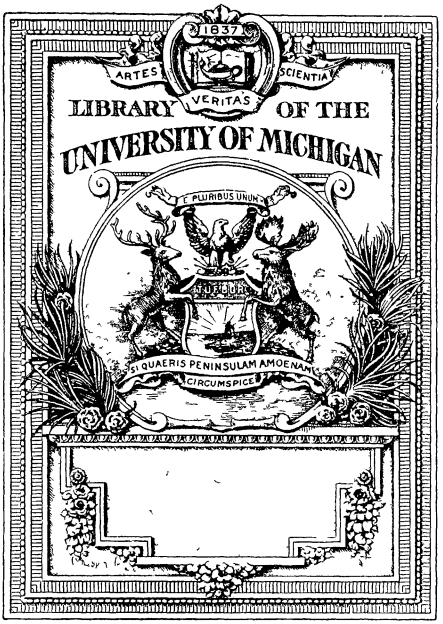

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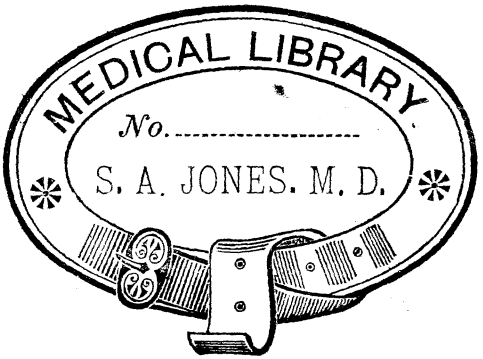

S. A. Jones, M. D.

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HANDBOOK

OF

MODERN CHEMISTRY

INORGANIC AND ORGANIC.

For the use of Students.

BY

CHARLES MEYMOTT TIDY, M.B., F.C.S.,

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Late Deputy Medical Officer of Health & Public Analyst for the City of London;
Master of Surgery, &c., &c., &c.

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TO

HENRY CLIFTON SORBY, F.R.S.,

President of the Geological Society, &c., &c.

48, QUEEN ANNE STREET,

CAVENDISH SQUARE, W.

April, 1878.

MY DEAR MR. SORBY,

Our long friendship would of itself be sufficient reason for my desiring to dedicate this work to you.

The high position you have attained in the scientific world adds, however, a deep sense of pride to my feeling of pleasure in seeing your name upon its opening page. Most truly do I wish that those who study its contents may find some slight reflection of that remarkable accuracy of thought and work, of which all that you have done and written affords so brilliant an example.

Believe me,

My dear Mr. SORBY,

Ever sincerely yours,

C. MEYMOTT TIDY.

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PREFACE.

WHEN an author writes a new book on a subject upon which so many good books have been already written, he is expected to give some reason for doing so.

I venture, therefore, to plead my apology for the publication of these outlines of Chemistry. Within three months of graduating—in other words, when "fresh from the schools"—I was appointed Joint Lecturer on Chemistry with the late Dr. Letheby, at the London Hospital. Consequently, my first lecture-notes were prepared when familiar by practical experience with the wants of a student. Year by year, these notes have been added to, and, to some extent, re-written; nevertheless, except in a few instances, I have strictly adhered to the general plan I first adopted. I submit these lecture-notes to the profession as the joint experience of a student and a teacher.

In the *first* section of this work, I have considered the chemistry of the non-metals; in the *second*, the chemistry of the metals; and, in the *third*, the chemistry of organic bodies.

Before proceeding to details, I have in each case generalized largely on the subject matter of the section. Thus, as introductory to the science of chemistry generally, and before describing the metalloids, I have discussed at some length the subject of chemical affinity. In a similar manner, I have generalized on the metals and on the chemistry of organic bodies, before proceeding to the consideration of the several elements or compounds comprehended under the sections. Nothing to my mind is more important than for teachers and students to grasp the notion that the lecture-room is not the same as the study—in other words, that the lecture will not take the place of the book.

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any more than the book can take the place of the lecture. Each has its own special work in education. Thus it appears to me that in the lecture-room the work of the teacher is best fulfilled by sketching accurately, yet broadly, the general outlines of the whole subject, intensifying them where necessary by illustration and experiment (in fact, so to speak, covering the canvas), leaving the student, in the quiet book-work of the study, to fill in the minute details for himself. With this view of the different functions of lectures and books, I have always adopted in the lecture theatre the system of broad generalization, such as I have briefly shadowed forth in the remarks introductory to the several sections. I hope these may prove of general use as an introduction to the detailed work that follows, but they are mainly intended as a guide to my own pupils at lecture.

Thus much for introductory generalization.

As regards the details, my aim has been to be methodical. I have therefore considered each element, and, as far as possible, each compound, under the several heads of (1.) History, (2.) Natural History, (3.) Preparation, (4.) Properties, (α.) Sensible, (β.) Physical, and (γ.) Chemical; (5.) Uses in Medicine and in the Arts and Manufactures, and (6.) Tests.

In dealing with the metalloids I have commenced with oxygen and finished with hydrogen, discussing under each element the compounds it forms with the elements previously considered in detail. Thus, for example, under hydrogen (the last of the metalloids), I have described all the compounds that it forms with the non-metals.

From page 437 to page 462 will be found the tables I am in the habit of employing in my practical chemistry class. Before considering the course to be adopted in the separation of the several groups, I have always insisted on the necessity of an accurate knowledge, not only of the reactions of each member of the group, but more particularly of the relationship between the reactions of the several members of the group with the same reagent. This I have attempted to set forth in a series of Tables. In respect of order (regarding classification as simply a question of convenience), I prefer beginning my practical course of lectures with the alkaline metals and working backwards.

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The reactions of the rarer metals are not included in the analytical tables, but they will be found in the body of the work under their several headings.

Bearing in mind the requirements of students preparing for examinations, I have described the reactions of organic bodies at the end of the several chapters devoted to their study. Thus the reactions of cyanogen compounds will be found on page 522; of the alcohols (together with the starches and sugars) on page 589; of the organic acids on page 626; and of the alkaloids on page 674.

As regards notation, although I recognise great advantages in that suggested by Dr. Frankland, I am by no means prepared to abandon the old formulæ. Under these circumstances I have, in the inorganic portion of the work, stated equations in both molecular and constitutional formulæ.

In the case of each metal I have drawn up a table of its most important compounds, their formulæ, and such tabulated information respecting them as I thought would prove useful to the student.

My first object in this book is that it should serve as a manual for students. As a medical man and a professor in a medical school, I have always made a special point in my lectures of noting the bearing of chemical science on medicine. This will account to the general student of chemistry for my dealing with certain subjects in a greater detail than is usual in similar works.

Further, bearing in mind the special knowledge required of medical officers of health in dealing with nuisances arising from various trade operations, I have given the outlines (limited of course to the strictly scientific details) of most manufacturing processes, and of the chemical reactions involved in the same. To cure a nuisance is more scientific than to annihilate a manufactory, and to suggest the cure we must accurately understand the case.

To the lecture-notes of Dr. Frankland and to the manuals of Chemistry of Odling, Williamson, Roscoe, Bloxam, Thorpe, Miller, and Fownes, and particularly to the excellent manual on Organic Chemistry by Dr. Armstrong, I desire to express my obligations.

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I should wish to add that, although I have spared no pains to render this Handbook as complete and as accurate as possible, nevertheless I trust that some allowance will be made for unavoidable errors arising from the circumstance that it has been written amidst the constant interruptions of professional work. Not unfrequently indeed has it had for a time to be laid aside altogether, thereby rendering continuity of thought and uniformity of treatment a matter of some difficulty.

48, QUEEN ANNE STREET,
CAVENDISH SQUARE.
April, 1878.

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TABLE OF THE ELEMENTS.

NOTE.—1. The page after the Elements refers to the page in the book where the Element is described.
2. The Metalloids are printed in Black type, and the Metals in Roman type.

Element.	Symbol.	Atomic Weight.	Atomicity.	Relative Weight H = 1.	Specific Gravity of Gas or Vapor Air = 1.	Specific Gravity of Solids and Liquids Water = 1.	Melting Point. ° F.	Boiling Point. ° F.	100 cubic inches of Gas or Vapor weigh in grams.	Discoverer and Date of Discovery.
Aluminium (p. 339)	Al	27·5	IV.			2·6	842·0			Wöhler, 1828.
Antimony (Stibium) (p. 388)	Sb	122·0	III., V.			6·7	806·0			Basil Valentine.
Arsenicum (p. 394)	As	75·0	III., V.	150	10·6	5·90	Volatilizes before fusing at 356.		329·13	Brandt, 1733.
Barium (p. 314)	Ba	137·0	II.			4·0	Below red heat			Davy, 1808.
Bismuth (p. 372)	Bi	210·0	III., V.			9·83	507·2			
Boron (p. 183)	B	11·0	III.			2·68				Davy, 1807.
Bromine (p. 83)	Br	80·0	I.	80·0	5·54	3·187	—4	145·4		Balard, 1826.
Cadmium (p. 376)	Cd	112·0	II.	56·0	3·94	8·604	442	1580	122·33	Stromeyer, 1818.
Cæsium (p. 309)	Cs	133·0	I.							Bunsen and Kirchhoff, 1860.
Calcium (p. 317)	Ca	40·0	II.			1·578	Red heat.			Davy, 1808.
Carbon (p. 166)	C	12·0	(II.) IV.			3·5				Pre-historic.
Cerium (p. 346)	Ce	92·0	II.							
Chlorine (p. 70)	Cl	35·5	I.	35·5	2·47	1·33			76·3	Scheele, 1774.
Chromium (p. 357)	Cr	52·5	(II., IV.) VI.			7·01				Vauquelin, 1797.
Cobalt (p. 333)	Co	58·8	II. (IV.) VI.			8·95				Brandt, 1733.
Copper (Cuprum) (p. 364)	Cu	63·5	II.			8·96	1996·0			Pre-historic.
Didymium (p. 347)	Di	96·0	II.							
Erbium (p. 346)	E	112·6	II.							
Fluorine (p. 69)	F	19·0	I.		1·318 (?)				40·87 (?)	Davy, 1808.
Gallium (p. 434)	Ga	69·9	IV.			5·935	86·27			Boisbaudran, 1875.
Glucinum (Beryllium) (p. 346)	G	9·5	II.			2·1				
Gold (Aurum) (p. 400)	Au	196·7	(I.) III.			19·4	2192·0			Pre-historic.
Hydrogen (p. 191)	H	1·0	I.	1·0	0·0693				2·1496	Cavendish, 1766.
Indium (p. 337)	In	113·4	III.			7·4				Reich and Richter, 1863.
Iodine (p. 86)	I	127·0	I.	127·0	8·716	4·947	225·0	347·0	270·32	Courtois, 1812.
Iridium (p. 435)	Ir	198·0	II., IV., VI.			21·15				Smithson Tennant.
Iron (Ferrum) (p. 347)	Fe	56·0	II., IV. (VI.)			7·79				Pre-historic.

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Lanthanum (p. 347)	La	92·0								Mosander, 1841.
Lead (Plumbum) (p. 410)	Pb	207·0	II. (IV.)			11·445	617·0			Pre-historic.
Lithium (p. 308)	Li	7·0	I.			0·593	356·0			Davy.
Magnesium (p. 322)	Mg	24·0	II.			1·743	Red heat.			Davy, 1808.
Manganese (p. 326)	Mn	55·0	II., IV. (VI.)			6·85				Gahn, 1780.
Mercury (Hydrargyrum) (p. 421)	Hg	200·0	II.	100·0	6·97	13·56	37·9	675·0	216·09	Pre-historic.
Molybdenum (p. 408)	Mo	96·0	II., IV., VI.							
Nickel (p. 335)	Ni	58·8	II., IV., VI.			8·9				Cronstedt, 1751.
Niobium	Nb	97·6	V.							
Nitrogen (p. 93)	N	14·0	I., III., V.	14·0	0·9713				30·137	Chaptal, 1789.
Osmium (p. 380)	Os	199·0	II., IV., VI.			21·4				Tennant, 1803.
Oxygen (p. 54)	O	16·0	II.	16·0	1·1056				34·27	Priestley, 1774.
Palladium (p. 377)	Pd	106·5	II., IV.			11·6	2480·0			Wollaston, 1803
Phosphorus (p. 122)	P	31·0	III., V.	62·0	4·290	1·848	112·0	554	133·23	Brandt, 1669.
Platinum (p. 403)	Pt	197·4	(II.), IV.			21·5				Wood, 1741.
Potassium (Kalium) (p. 289) ..	K	39·0	I.			0·865	144·5	Low red heat.		Davy, 1807.
Rhodium (p. 379)	Rh	104·3	III., VI.			12·1				Wollaston, 1803.
Rubidium (p. 309)	Rb	85·4	I.			1·52				Bunsen and Kirchhoff, 1860.
Ruthenium (p. 381)	Ru	104·4	II., IV., VI.			11·4				Claus, 1846.
Selenium (p. 162)	Se	79·5	II., IV., VI.	79·5	5·68	4·788	212·0		176·08	Berzelius, 1817.
Silicon (p. 185)	Si	28·5	IV.			2·0				Davy, 1807.
Silver (Argentum) (p. 416)	Ag	108·0	I.			10·50	1681·0			Pre-historic.
Sodium (Natrum) (p. 297)	Na	23·0	I.			0·972	207·7			Davy, 1807.
Strontium (p. 316)	Sr	87·6	II.			2·54				Davy, 1808.
Sulphur (p. 143)	S	32·0	II., IV., VI.	32·0	2·222 at 1040° C.	2·05	239·0	836·0	68·76	Pre-historic.
Tantalum	Ta	182·0	IV.							
Tellurium (p. 164)	Te	128·0	II., IV., VI.	128·0	9·0	6·2	900		279·0	Müller, 1782.
Thallium (p. 430)	Tl	204·0	I., III.			11·91	561	Below white heat.		Crookes, 1861.
Thorinum (*or* Thorium) (p. 347)	Th	231·5	II., IV.			7·8				Berzelius, 1829.
Tin (Stannum) (p. 383)	Sn	118·0	II., IV.			7·28	442·4			Pre-historic.
Titanium (p. 361)	Ti	50·0	II., IV.			5·3				Gregor, 1891.
Tungsten (Wolfram) (p. 432) ..	W	184·0	IV., VI.			17·4				
Uranium (p. 336)	U	240·0	II., IV., VI.			17·6				Klaproth.
Vanadium	V	51·3	V.							
Yttrium (p. 346)	Y	61·7	II.							
Zinc (p. 330)	Zn	65·0	II.	32·5		6·8—7·2	773·0	1,904		In 13th Century.
Zirconium (p. 347)	Zr	89·5	IV.			4·15	Infusible.			

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A

HANDBOOK OF MODERN CHEMISTRY.

CHAPTER I.

CHEMICAL AFFINITY.

Definition—Conditions necessary for its exertion—Phenomena—The circumstances influencing its action—The means of estimating the energy of the force.

AFFINITY may be defined as 'a force of attraction acting between two or more *dissimilar* particles brought together at an *inappreciable distance*, whereby a new compound is formed, having *properties different from those of its constituents*.' Thus, if we effect a chemical combination between *Iodine* (a black, poisonous substance) and *Potassium* (a silvery white metal) we obtain a compound (Potassic Iodide) which bears no resemblance sensibly, chemically, physically, or physiologically to either of its constituent elements. This change of property is the special characteristic of Chemism or Chemical Affinity. In *gravitation* we have attraction between similar or dissimilar molecules, at an appreciable distance; in *cohesion*, attraction between similar molecules at an inappreciable distance; in *adhesion*, attraction between dissimilar molecules at an inappreciable distance; but in none of these attractive forces have we any change in the matter on which the force is exerted.

The chemical force has been designated by different names: Bergman called it "*Elective Gravitation*;" Azais "*Molecular Gravitation*;" Newton "*Chemical Attraction or Action*;" others "*Heterogeneous Affinity*;" whilst Stahl invented the name "*Chemical Affinity*" or simply "*Affinity*," with the idea that bodies that combined chemically had some common resemblance. ("Like consorts with like."—*Hippocrates.*) In employing the term Affinity as a name for the force, we do not accept the grounds upon which it was originally adopted; for, chemically, like does not consort with like, but, *par excellence*, with unlike; bodies the most opposite, as, for example, acids and alkalies, being invariably the most disposed to combine.

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I. The Conditions necessary for the Exertion of Affinity.

(*a.*) *There must be two or more dissimilar particles.*—There can be no chemical union between iron and iron, or between sulphur and sulphur, but iron and sulphur are capable of chemical combination. Further, the more completely the substances are chemically unlike, the more intense usually is the play of affinity. The constituents of most chemical compounds, when subjected to an electric current, pass to opposite poles—those attracted to the *positive* pole of the battery being termed *electro-negative* elements, and those attracted to the *negative* pole, *electro-positive* elements. Two positive or two negative elements may, and under some circumstances do, combine, but the chemical phenomena resulting from such combinations are usually so slight, that at times it is difficult to say whether such compounds are not purely molecular or mechanical.

In affinity, moreover, we note a certain *elective power*. If, *e. g.*, hydrochloric acid be poured on lime and alumina, upon both of which it is capable of acting, we find that the acid acts by preference on the lime ("Elective Affinity" of Bergman).

(*β.*) *The particles concerned must be brought into absolute contact.*—This may be effected by various agencies, such as heat, solution, or mechanical action.

II.—The Phenomena of Affinity.

All the phenomena of affinity are indicative of change. In *a mechanical mixture* the constituents are not changed, and consequently the nature of the compound is a mixture of the natures of the constituents. In *a chemical mixture* the properties of the compound may bear no resemblance whatsoever to the properties of the constituents of which it is composed. Thus we notice, as the results of affinity, changes in the *sensible*, the *physiological*, the *physical*, and the *chemical* properties of bodies.

(A.) Changes in the Sensible Properties.

(*a.*) *Color:* This may be—

(1.) *Produced;* (Example) Solutions of potassic iodide and plumbic acetate (both of which are colorless) produce, when mixed, the yellow plumbic iodide.

(2.) *Altered;* (Example) The action of an acid on litmus, or of an alkali on turmeric.

(3.) *Destroyed;* (Example) Action of chlorine on indigo.

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(β.) *Odor:* This may be—

(1.) *Produced;* (Example) Sulphuretted hydrogen, a compound of sulphur and hydrogen.

(2.) *Altered;* (Example) Nitro-benzene formed by the action of nitric acid on benzene.

(3.) *Destroyed;* (Example) Action of chlorine on sulphuretted hydrogen.

(γ.) *Taste:* This may be—

(1.) *Produced;* (Example) Nitrogen and hydrogen form ammonia.

(2.) *Altered;* (Example) Chlorine and sodium form common salt.

(3) *Destroyed;* (Example) Baric oxide and sulphuric acid form the tasteless baric sulphate.

(B.) CHANGES IN THE PHYSIOLOGICAL PROPERTIES.

(α.) *Harmless bodies become active*—

Example (1.) Strychnia, a deadly poison, is formed by the combination of the harmless bodies, carbon, hydrogen, oxygen and nitrogen.

(2.) Sulphuric acid, a corrosive poison, is formed by the combination of the inert bodies, sulphur, hydrogen, and oxygen.

(β.) *Active bodies become inert.*—This is the principle of antidotes; sulphuric acid is a poison, but if this be combined with calcic hydrate, the inert body calcic sulphate is formed.

(C.) CHANGES IN THE PHYSICAL PROPERTIES.

(α.) *Aggregation*—

(1.) Solids become liquids; (Example) Sulphur and carbon form carbonic disulphide CS_2.

(2.) Solids become gases ; (Example) Gunpowder when heated produces a gas.

(3.) Liquids become solids; (Example) Solid carbon is set free by the action of sulphuric acid on strong syrup.

(4.) Liquids become gases ; (Example) Effervescence.

(5.) Gases become solids; (Example) Ammonia gas and hydrochloric acid gas form solid ammonic chloride.

(6.) Gases become liquids ; (Example) Hydrogen and oxygen form water, OH_2.

(β.) *Density.*—The density of bodies is usually increased by affinity. If 1 volume of alcohol (Sp. Gr. 0·796) be mixed with 1 volume of water (Sp. Gr. 1·0) a liquid is produced having a Sp. Gr. of 0·917, whereas the mean Sp. Gr. would be 0·898.

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Various other properties are also changed along with density, such as the hardness of a body, its sonorousness, etc.

(γ.) *Changes in the thermotic properties of bodies.*

(i.) *Temperature.*—Heat is usually if not always produced as the result of affinity. The heat evolved may be very slight, as when an alkaline sulphate is added to baric nitrate; whilst it may result in combustion, where the evolution of light and intense heat are accompanying phenomena. Cases where cold apparently results from chemical combination are exceptional, and are always more or less accompanied by the phenomena of fluidity, the heat required to effect the change of the solid to a liquid being in excess of the heat produced.

(ii.) *Fusibility.*—With few exceptions the chemical compound is more fusible than the mean fusibility of the constituents.

(1.) *Fusibility increased.*—A mixture of 1 part of lead, 1 of tin, and 2 of bismuth, melts at 167° F. (75° C.), whereas the mean melting point of the constituents would be 512° F. (267° C.).

(2.) *Fusibility diminished.*—Such cases are rare. The metallic sulphides supply us, however, with illustrations.

(iii.) *Volatility.*—This may be increased or diminished;—

(1.) *Volatility increased.*—When carbon (a non-volatile body) is combined with sulphur, which is volatile at 600° F. (316° C.), carbonic disulphide (CS_2) is formed, which is a liquid that has never been frozen, is volatile at ordinary temperatures, and boils at 111° F. (44° C.).

(2.) *Volatility diminished.*—Water boils at 212° F. (100° C.). In some chemical compounds, however, it is absolutely non-volatile.

So again the electrical states and the crystalline forms of bodies are altered by the action of affinity.

III.—Circumstances Influencing Chemical Affinity.

Inasmuch as affinity depends on molecular attraction, it follows that whatever tends, on the one hand, to bring the particles together, or, on the other hand, to separate them, must influence the action of the force; in the former case aiding, and in the latter case preventing it.

1. Gravitation Modifies Chemical Action.

Gravity affects affinity by the disposition of the heavier particles to sink, and of the lighter particles to rise to the surface.

2. Cohesion Modifies Chemical Action.

Affinity being a molecular force, it follows that it will be favoured by any means that lessen cohesion, such as mechanical division (powdering), heat (fluidity), or solution. Cohesion may for a time overrule affinity, affinity coming into play immediately the cohesion is broken down. The action of cohesion in influencing the force may be either exerted upon the constituents or upon the resultant.

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(*a.*) *Cohesion of the Constituents.*—A lump of lead is very slowly acted upon when exposed to the air, but if it be in a finely powdered state (*pyrophoric*) it instantly ignites. If finely powdered antimony be introduced into chlorine it takes fire, but this intense chemical action does not occur when a lump of the metal is placed in the gas.

(*β.*) *Cohesion of the Resultant.*—When sulphuric acid is added to a baric nitrate solution, baric sulphate is precipitated. The sulphuric acid thus removes the barium out of the sphere of chemical action, by reason of the superior cohesion of the resultant. This action is often attributed to what is called *superior affinity*, but there are difficulties in admitting this as an explanation in such cases, owing to the capricious action of the force. For example, if acetic acid be added to a solution of potassic carbonate in *water*, carbonic anhydride escapes, and potassic acetate is formed; but if carbonic anhydride be passed through a solution of potassic acetate in *spirit*, acetic acid is set free and potassic carbonate is formed, which, being insoluble in the spirit, is precipitated.

We may here consider—

(A.) *The action of acids on salts in solution.*

(*a.*) If an acid be added to a solution of a salt, such acid being of nearly equal chemical power to the acid of the salt, and with the base of which salt it can unite to form a soluble compound, the probability is that the base will be divided between the two acids, equally or unequally, both acids being also present in solution in the free state.

Example: Sulphuric acid + potassic nitrate = potassic sulphate + potassic nitrate + sulphuric acid + nitric acid.

(*b.*) If an acid be added to a solution of a salt, such acid being of much greater chemical activity than the acid of the salt, but with the base of which salt it can unite to form a soluble compound, the strong acid will then appropriate the whole of the base, and set free the whole of the acid originally combined with the salt.

Example: Sulphuric acid + sodic biborate = sodic sulphate + boric acid.

(*c.*) If an acid be added to a solution of a salt, aqueous or otherwise, it being immaterial whether the acid so added be of greater or of less chemical power than the acid present in the salt, but with the base of which salt it is capable of forming a precipitate insoluble in the menstruum in which the salt is dissolved; the acid added will appropriate the whole of the base, and set free the original acid.

Examples (1) Sulphuric acid + baric nitrate = baric sulphate + nitric acid.
(2) Hydrocyanic acid + argentic nitrate = argentic cyanide + nitric acid.
(3) Tartaric acid + argentic sulphate = argentic tartrate + sulphuric acid.

(*d.*) If to a solution of a salt, the acid of which is insoluble in the menstruum in which the salt is dissolved, an acid be added which forms with the base of the salt a soluble salt, the acid added will then

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combine with the whole of the base, whilst the acid previously in combination with it will be precipitated.

Example: Nitric acid + potassic tungstate = potassic nitrate + tungstic acid.

(B.) *The action of bases on salts in solution.*

(*a.*) If to a solution of a salt, the base of which is soluble, another base be added which is also soluble and capable of forming a soluble salt with the acid of the original salt, the acid will then be divided between the two bases in proportion to its affinity for each.

Example: Potassic hydrate + sodic nitrate = sodic nitrate + potassic nitrate + sodic hydrate + potassic hydrate.

Note further that in some cases a portion of the base may be precipitated, owing to its somewhat imperfect solubility.

Example: Potassic hydrate + baric nitrate = potassic nitrate + baric nitrate + potassic hydrate + baric hydrate (a portion of which will be precipitated).

(*b.*) If to a solution of a salt, the base of which salt is entirely insoluble, a base be added which forms a soluble salt with the acid of the original salt, then the base of the original salt will be precipitated, and the whole of the acid set free will combine with the new base added.

Example: Ammonia + ferric sulphate = ferric oxide + ammonic sulphate.

This rule has its exceptions; ammonia will not throw down the base of mercuric cyanide, although it is insoluble.

(*c.*) If to a solution of a salt a base be added, which with the acid of the salt forms an insoluble compound, all the acid of the original salt will be precipitated with the newly added base, the other base if soluble remaining in solution.

Example: Baric hydrate + potassic sulphate = baric sulphate + potassic hydrate.

(*d.*) If to a solution of a salt, the base of which is insoluble, a base be added which forms an insoluble compound with the acid of the original salt, both bases, as well as the acid previously in contact with the one base, will be precipitated from the solution.

Example: Baric hydrate + argentic sulphate = baric sulphate + argentic hydrate.

(C.) *Action of salts on salts in solution.*

(*a.*) If a soluble salt be added to a soluble salt, both salts, by a mutual interchange of acids and bases also forming soluble salts, a solution of four salts in unknown proportions will probably result.

Example: Potassic sulphate + sodic nitrate = potassic sulphate + potassic nitrate + sodic sulphate + sodic nitrate.

(*b.*) If a soluble salt be added to a soluble salt, both salts by a mutual interchange of acids and bases forming an insoluble or sparingly soluble salt, decomposition will result, and the compound that is least soluble will be precipitated.

Example: Argentic nitrate + sodic chloride = argentic chloride + sodic nitrate (the argentic chloride being precipitated).

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3. Elasticity Modifies Chemical Action.

Elasticity (that is, the absence of cohesion) bears a close relationship in its action upon affinity to cohesion (that is, the absence of elasticity). Both are capable of effecting the removal of bodies from compounds; cohesion, by reason of the insolubility of certain bodies, and elasticity by reason of the volatility of others. But, although the action of the two forces are thus *analogous*, they are often *opposite*. If, for example, we add ammonia to a solution of magnesic sulphate, magnesia is precipitated, and ammonic sulphate remains dissolved. This precipitation of magnesia is the action of *cohesion*. But if dry ammonic sulphate and dry magnesia are heated together, ammonia is expelled and magnesic sulphate is formed. This evolution of ammonia is the action of *elasticity*. It is the spring of repulsion between the particles, or, in other words, the distance maintained between the particles (elasticity) which prevents hydrogen and oxygen combining, but when this repulsion or distance is overcome by some such power as pressure, heat, or the action of spongy platinum, combination immediately results. Thus elasticity is made use of by the chemist for the purpose both of breaking up old compounds and of producing new ones. Acids, bases, and salts are all more or less affected by its action;—Thus

(*a.*) *Acids.*—If an acid be added to a salt containing an acid capable either of assuming a gaseous form at ordinary temperatures, or of being converted into vapour at a temperature below that required to volatilise the acid added to displace it, the acid in the salt will be driven off and a new compound formed, consisting of the base of the original salt with the new acid. For example, if we add to a carbonate any acid except hydrocyanic or hydrosulphuric acid, the carbonic anhydride of the salt is immediately evolved, owing to its elasticity. Thus—

Potassic carbonate + sulphuric acid = potassic sulphate + carbonic anhydride.

Again: Sulphuric acid displaces nitric, hydrochloric, acetic, formic, butyric, and other volatile acids from their salts during distillation.

Further, it is to be noted that whatever tends to increase the elasticity of a body, such as heat, will also favour or modify chemical action. This circumstance explains certain contradictory phenomena, whereby salts of strong acids are decomposed by the action of weak acids. For example—sulphuric acid has a strong affinity, and boracic acid a weak affinity for bases. If sulphuric acid be added to a solution of sodic borate, boracic acid is set free, and sodic sulphate is formed. But if sodic sulphate and boracic acid be fused together, sulphuric acid is volatilised (elasticity) and sodic borate is formed. The same is also true of the action of silicic and phosphoric anhydrides on the sulphates. Or, again, if oxalic acid be boiled with a solution of a chloride, hydrochloric acid will be expelled from the

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solution. Thus it will be noted that a feeble acid may drive off a strong acid, provided that the stronger acid be the more volatile of the two.

(*β.*) *Bases.*—If a salt of a volatile base be heated with a fixed base, the fixed base displaces the volatile base. For example: If an ammonic salt be heated with calcic or potassic hydrate, a salt of the new base is produced, and ammonia gas evolved. Here, again, contradictory phenomena may be noted. For if ammonia be added to an aluminic sulphate solution, alumina is precipitated and ammonic sulphate formed; but if dry alumina and dry ammonic sulphate be heated together, ammonia is evolved and aluminic sulphate formed.

(*γ.*) *Salts.*—Reactions of a similar nature occur in the case of salts. If a solution of ammonic carbonate be added to a solution of calcic chloride, calcic carbonate is precipitated and ammonic chloride remains in solution; whilst, on the contrary, if dry ammonic chloride and dry calcic carbonate be heated together, ammonic carbonate is evolved and calcic chloride remains.

The power of elasticity on affinity is curiously influenced by certain mechanical processes whereby the components of the body undergoing change are removed from the sphere of action. For example—If ferric oxide be heated in a current of hydrogen, the iron is reduced, the little steam formed being carried away by *the excess of hydrogen;* whilst if metallic iron be heated in a current of steam, the water is decomposed, ferric oxide is formed, and the hydrogen liberated is carried away by *the excess of steam.*

Further chemical action may be retarded if the escape of bodies be prevented by mechanical means. For example, if an acid be poured on calcic carbonate in a flask provided with a stopcock, the stopcock being open, carbonic anhydride escapes, owing to its elasticity, and a new lime salt with the acid is formed; but the escape of the acid, and the consequent formation of the new salt will be impeded if the stopcock is closed, the action again proceeding when it is reopened.

Again, if calcic carbonate (as in a lime kiln), be heated *exposed to the air,* all the carbonic acid is driven off, and quick lime (CaO) remains. But if calcic carbonate be heated in a *closed* tube, so that the escape of the carbonic anhydride is prevented, it may be fused without decomposition resulting.

4. Adhesion Modifies Chemical Action.

Just as cohesion opposes, so adhesion invariably assists affinity. Nor is this other than would be expected, when we remember the close relationship subsisting between affinity and adhesion, it being often difficult to mark the exact line dividing them. The powerful influence of solution (*i. e.* adhesion of liquids and solids or liquids and gases), in aiding affinity has been already referred to. As an

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example—baric nitrate is soluble in water as well as in *dilute* nitric acid, but is insoluble in *concentrated* nitric acid. If strong nitric acid be poured on baric carbonate, no action results; but if water be added to the mixture, carbonic anhydride is evolved, and baric nitrate remains in solution. The chemical action in this case did not occur until circumstances favoured solution. So also an alcoholic solution of an acid (as tartaric acid) will not decompose a carbonate (as potassic carbonate), unless the resulting salt is soluble in alcohol. If dry sulphuretted hydrogen be mixed with dry sulphurous anhydride they will not act, whilst decomposition is immediate if moisture be present.

(*a.*) *Adhesion of gases to solids (surface action).*—If a piece of porous charcoal be introduced into ammonia gas standing over mercury, the charcoal, by reason of the force of adhesion between itself and the gas, condenses the gas in its pores. The action of spongy platinum in effecting the combination of mixed hydrogen and oxygen gases, and the ease with which a piece of platinum foil may be kept red hot by allowing a jet of coal gas to play upon it, are further illustrations of the power of adhesion in aiding affinity. In this latter case we may regard *the elastic force* of the gases as the cause preventing their union. The platinum, however, by effecting a condensation of the gases upon its surface, brings them within the range of each other's chemical attraction (Faraday). This being so, it will be understood that the larger the surface exposed, the greater the condensation. Hence the more intense action of platinum when finely divided, as in the state of platinum black. In this power of adhesion, moreover, we have the means of effecting chemical combinations otherwise unprocurable. For example, spongy platinum will coerce the formation of water and nitric acid from ammonia and air—a reaction impossible to effect by heat alone,—whilst ammonia may be formed from the oxides of nitrogen and hydrogen in a similar manner. Sulphurous anhydride may be oxidised by the action of spongy platinum, to sulphuric anhydride—a process which has been suggested as a means of preparing sulphuric acid. Nor is this action peculiar to platinum; in an inferior degree gold, silver, palladium, iridium and other metals having no strong affinity for oxygen, (for otherwise the surface of such metals would soon become oxidized), act similarly. This action is modified and often entirely stopped by the presence of minute quantities of certain vapours and gases, such as, *e. g.*, carbonic oxide, vapour of carbonic disulphide, phosphoretted hydrogen, sulphuretted hydrogen, etc.

(*β.*) *Action of nascent matter.*—If hydrogen be generated in the presence of arsenious acid, it combines with the arsenic to form arseniuretted hydrogen. But its power of combining with the arsenic is limited to the instant of its being set free, for, if the hydrogen, immediately after being generated, be conveyed through a solution

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of arsenious acid, no such combination will be found to result. Again, if a stream of hydrogen be passed through a mixture of argentic chloride and water, no action on the silver salt will be apparent; but if the hydrogen be generated *in the presence* of argentic chloride, the silver will be instantly reduced.

Again, in the colour tests for morphia, strychnia, or aniline, it is essential that the oxygen be generated in the presence of these bodies. This is commonly effected by the action of sulphuric acid on some salt, such as potassic bichromate, or by the oxygen liberated at the positive pole of the battery. But by whatever means we set free the oxygen, the gas must be *nascent*, that is, the bodies upon which it is to act must be present at the moment of its birth.

We may suppose in such cases that the gases are for a moment under coercion, or in other words, that the elasticity of the gases has not yet come into play. In such a condition, chemical combinations may be easily effected.

5. Influence of Mass or Quantity on Affinity.

It will be remarked, that if one body unites with another body in several proportions, the compound which possesses the smallest number of elements is generally the most difficult to decompose. For example, if plumbic dioxide (PbO_2) be heated, it becomes plumbic oxide (PbO), but a continuance of the same heat will not decompose the plumbic oxide.

We have now to examine this subject from another point of view.

If we add an equivalent of sulphuric acid to a solution of potassic nitrate, we have said that a mixture of potassic sulphate and potassic nitrate will be formed, together with free acids. Suppose we add, however, *a great excess* of sulphuric acid, the question is, Will this excess influence the relative quantities of the two salts formed? This subject was first investigated by Berthollet, who deduced the law "*that in elective attraction the power exerted is not in the ratio of the affinity simply, but in the ratio compounded of the force of affinity and the quantity of the agent.*" That is, in other words, that quantity may be made to compensate for a weaker chemical action. Gladstone has further investigated this subject, employing the change of color brought about by affinity (as by the action of potassic sulphocyanide on ferric salts) as a means of determining the extent of the decomposition. The fact was demonstrated that if a quantity of potassic sulphocyanide be mixed with ferric nitrate, the quantity of sulphocyanogen of the former being exactly equivalent to the iron of the latter, the whole of the iron was not withdrawn as ferric sulphocyanide; but that if a second equivalent of potassic sulphocyanide be added, more ferric sulphocyanide was formed, and so on with a third and a fourth equivalent, up to 375 equivalents, although, judging by the color,

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the effect of every addition became less and less. Gladstone concludes that mutual interchange takes place in determinate proportions, *independent* of the combination of the compounds, but *dependent* on the mutual strength of their affinities and on the proportions of each constituent present.

The effects of quantity in the combinations of gases, have also been investigated by Bunsen and Debus. Mixtures of hydrogen, oxygen, and carbonic oxide, in various proportions, the hydrogen and carbonic oxide being always in excess, were fired, and the relative proportions of water and carbonic anhydride formed, estimated. These were found to be dependent on the preponderation of the carbonic oxide, in accordance with an ascertained law. Harcourt and Essen have further investigated this influence of quantity, and agree in the general conclusion that chemical affinity is affected by quantity or mass.

6. Mechanical Force may modify Chemical Action.

Pressure, percussion, friction, agitation, and indeed all forms of mechanical action influence the chemical force, both by disturbing and by favoring its manifestation. A solution of tartaric acid added to a solution of potassic chloride needs to be well stirred in order to secure the complete formation of the potassic tartrate. This, as well as numerous other cases where the stirring-rod is so constantly in requisition in the laboratory, illustrates the influence of mechanical action on affinity.

On the other hand, mechanical action may destroy the force. A touch, *e.g.*, disturbs the equilibrium of the particles of iodide of nitrogen. The fulminating compounds need simply a blow to break them up. This is indeed the history of explosions generally.

7. Contact Decomposition.—Ferments.—Catalysis.

Certain bodies exert on other bodies by their mere contact (*i.e.*, by the action of presence) a power whereby the decomposition of the body is effected, and new compounds are formed. The substance which excites this action (*i.e.*, the ferment) neither gives anything to the compound on which it acts, or takes anything away from it.

Illustrations of contact decomposition may be noted in the following cases :—

(1.) Hydric peroxide (H_2O_2) is a powerful oxidizing agent. If, however, finely divided metallic gold, silver, or platinum be added to the liquid it will suffer decomposition, although the metal itself will undergo no change. Further, if instead of employing metallic gold or silver, auric or argentic oxide be placed in the liquid, not only will the hydric peroxide be decomposed, but the metallic oxide itself will suffer decomposition and the metal be reduced.

(2.) Again, potassic chlorate is decomposed at 698° F. (370° C.),

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and liberates oxygen. If, however, the potassic chlorate be mixed with manganic peroxide or with cupric oxide and heated, the oxygen will be given off at a temperature of from 446° to 500° F. (230° to 360° C.), although the manganic peroxide itself undergoes no change.

(3.) Nitric acid converts starch into oxalic acid ($H_2 C_2 O_4$), but in the presence of a manganese salt, carbonic anhydride is formed.

(4.) *Sugar*, under the influence of yeast, breaks up into alcohol and carbonic anhydride, the yeast neither giving anything to, nor taking anything from, the sugar.

(5.) *Starch* in the presence of diastase is converted into sugar, a change which takes place in every germinating seed.

(6.) *Amygdaline* in the presence of synaptase (an albuminoid principle present in the pulp of the seed) breaks up into hydrocyanic acid, oil of bitter almonds, sugar, and formic acid.

These three last illustrations are regarded as cases of fermentation. The bodies capable of effecting the changes (ferments) in no way, however, contribute to the new products, although they themselves undergo specific changes during the process.

The theories to account for these phenomena will be discussed under fermentation. Berzelius imagined them due to a new force, which he designated *Catalysis*. Catalysis means fermentation, and the explanation of Berzelius is little else than "that fermentation is fermentation." Liebig imagined that they might be explained by supposing that the motion in the atoms of one body were communicated to the atoms of another body, thereby setting up similar changes, just as one body on fire is able to set on fire other bodies. Very frequently, however, the body that starts the fermentation, and the body that ferments, undergo vastly different changes. In such cases as 1, 2, and 3 given above, to which the term "*concurring attractions*" has been given, the catalytic body may, and possibly does, play a part, but what part is not exactly known. In case 1 Brodie has shown that there is a direct relationship between the quantity of the metallic oxide reduced and the hydric peroxide decomposed, and he supposes that the particles of the same element may attract one another, the atoms being in different electrical states. Liebig considered that various diseases, such as the Exanthems, were due to the contact of germinal matter (acting as a ferment) with substances in the blood capable of undergoing fermentation. The materials in the blood capable of being thus split up being exhausted, the disease could not, as he explained, again recur.

At present we class these phenomena together, awaiting further investigation, regarding the doctrine of Catalysis as a convenient fiction.

8. Influence of Heat and Cold on Affinity.

The chemical force acts only within a given range of temperature, the limits differing with different bodies. A red-hot glass rod, *e.g.*,

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will effect the combination of oxygen and hydrogen, whilst a white heat is necessary to decompose the compound so formed, into oxygen and hydrogen (*Phil. Trans.*, 1847). Mercury, when exposed to the action of oxygen at 698° F. (370° C.) forms mercuric oxide (HgO), whilst mercuric oxide at a higher temperature is again resolved into mercury and oxygen. Baric oxide (BaO) at *a red heat* becomes baric peroxide (BaO_2), but at *a white heat* baric peroxide is resolved into oxygen and baric oxide (BaO). Thus it is clear that a high temperature may undo the work done at a lower temperature.

(α.) *Heat may promote affinity.*—It does so by overcoming the force of cohesion. Thus an extreme cold, as, for example, the cold produced by a bath of ether and sodic carbonic anhydride(—104·8° F., or—76° C.) will prevent the combination of iodine and phosphorus, or of chlorine and phosphorus, or of chlorine and finely powdered antimony, but these bodies will severally combine on exposing them to ordinary temperatures. At common temperatures, again, sulphur will not combine with carbon, whilst at a high temperature the union of these bodies may be easily effected.

(β.) *Heat may destroy affinity.*—It does so by effecting a separation of the ultimate particles of the body. Probably, indeed, all substances would be decomposed if we could apply sufficient heat. Ammonia may be decomposed by heat. At a red heat C_4H_4 is decomposed into carbon and C_2H_4, whilst this latter at a higher temperature may be further decomposed into hydrogen and carbon.

To the *partial* decomposition of some bodies at a high temperature Deville has given the name "*dissociation.*" Thus, if steam and carbonic anhydride be passed through a red-hot porcelain tube, the gases left after the un-decomposed carbonic anhydride has been absorbed by potash will be found to be an explosive mixture of oxygen, hydrogen, and carbonic oxide, the hydrogen of the steam at the moment of its liberation from the oxygen, reducing a portion of the carbonic anhydride. Even the partial reduction of carbonic anhydride itself into carbonic oxide and oxygen may be effected by passing it through a porcelain tube heated to 2372° F. (1300° C.) Again, carbonic oxide may be partially resolved into carbon and carbonic anhydride by passing it through a heated porcelain tube, in the axis of which is placed a small and hollow brass tube kept cool by a constant current of water within, and upon which the carbon will be deposited. In a similar manner sulphurous anhydride may be partially resolved into sulphuric anhydride and sulphur.

(γ). *Heat modifies chemical action.*—In other words, the nature of the products may be influenced by the temperature. Thus, carbonic anhydride and water are formed by the combustion of ether in air, and carbonic anhydride and nitrogen by the combustion of cyanogen. But if a platinum wire be allowed to glow in a mixture of air and ether, aldehyde and acetic acid will be formed, whilst if the glowing

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platinum wire be placed in a mixture of cyanogen and oxygen, nitric oxide, and not nitrogen, will be produced.

9. Influence of Light on Affinity.

Light both promotes and destroys chemical action.

(α.) *Light promotes chemical action.*—Thus, chlorine and hydrogen will not combine in the dark, but in direct sunlight they combine with explosion. Chlorine and carbonic oxide under the influence of light combine to form phosgene, or light-formed gas.

(β.) *Light destroys chemical compounds.*—Thus, photography depends on the power of light to decompose argentic chloride. Sun-light again decomposes nitric acid, oxygen being evolved, the nitrous acid formed communicating a yellow tint to the acid.

10. Influence of Electricity on Chemical Action.

(α.) *Electricity promotes chemical combination.*—Dilute sulphuric acid has no action on the amalgamated zinc of a battery until a current is set up by bringing the poles together.

(β.) *Electricity both alters and destroys chemical combinations.*—Thus Davy decomposed the alkalies by electricity, and in this manner obtained the alkaline metals. When the galvanic current is passed through water it is split up into its constituent gases.

11. Influence of Vital Force on Chemical Action.

This influence is manifest in every living organism from the production of a simple cell to the highest manifestations of life. Elements are re-arranged under the influence of life to form the constituents of the organism, and out of a single fluid all the elements of growth and nutrition are elaborated, whilst the various secretions (mucous, bile, urine, milk, etc.), have their compositions determined by the agency of the vital force.

Thus it would seem that all forms of force influence affinity. The influence depends on their power respectively either to draw particles nearer together, thus promoting affinity, or to separate them, thus retarding or preventing it.

IV.—Degree, Force, or Energy of Affinity.

There is a great inequality in the action of affinity. The want of energy between oxygen and fluorine, and the intensity of energy between oxygen and potassium, is an illustration. The more opposite the bodies on which affinity is brought to bear, the more intense is its energy. If an iron rod be placed in a copper salt, the copper is thrown down on the iron, manifestly because the acid has a greater affinity for the iron than it has for the copper. Bergman termed the force of affinity *an elective force*, but he entirely overlooked the modifying influences of cohesion and elasticity. Berthollet, who pointed

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out these modifying influences, insisted that these were the forces that determined chemical decompositions.

Can we estimate, then, the amount of affinity between different bodies? Not *absolutely*, but, to a certain extent, *relatively*. Several methods have been proposed.

(1.) Affinity Measured by Reference to the Specific Gravity of Bodies (Laplace and others).

Acetic acid (Sp. Gr. 1·063)	poured on	carbonates	turns out	carbonic acid.
Hydrochloric acid (Sp. Gr. 1·247)	,,	acetates	,,	acetic acid.
Nitric acid (Sp. Gr. 1·421)	,,	chlorides	,,	hydrochloric acid.
Sulphuric acid (Sp. Gr. 1·60)	,,	nitrates	,,	nitric acid.

Thus it would seem that the greater the specific gravity of the acid, the more intense is its chemical action. But when we examine the alkalies we shall find that their energy of action, as shown by their specific gravity, is almost in an inverse order. Thus:—

Baryta...	5·456
Magnesia	3·60
Lime	3·180
Potash...	2·20
Soda	2·13
Ammonia solution	0·90

Thus it is manifest that specific gravity affords no test of the relative power of the force.

(2.) Affinity Measured by the Force of Adhesion (Guyton Morveau).

Guyton Morveau, who first suggested adhesion as a test of the energy of affinity, acted under the impression that adhesion was the first stage of affinity. He employed equal-sized discs of different metals suspended from one end of a scale beam, and estimated the weight necessary to separate them respectively from a layer of mercury. These weights he regarded as the measure of their affinity.

Affinity Measured by Adhesion (Guyton Morveau).

Gold	adheres to	Mercury	with a force of	446	grains.
Silver	,,	,,	,,	429	,,
Tin	,,	,,	,,	418	,,
Lead	,,	,,	,,	397	,,
Bismuth	,,	,,	,,	372	,,
Platinum	,,	,,	,,	282	,,
Zinc	,,	,,	,,	204	,,
Copper	,,	,,	,,	142	,,
Antimony	,,	,,	,,	126	,,
Iron	,,	,,	,,	115	,,
Cobalt	,,	,,	,,	8	,,

Achard followed out the same principle in greater detail, by using other solids and fluids. Gay Lussac estimated the force required to

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separate a circular glass disc (4·6 in. diameter) from the following fluids, and found it as follows:—

From water	... (Sp. Gr. 1·000)—	814·7 grains.
,, turpentine	(Sp. Gr. 0·869)—	523·6 ,,
,, alcohol	(Sp. Gr. 0·819)—	474·4 ,,

But there were manifest objections to this as a test of affinity:—

(1.) It was not a measure of affinity at all, but of adhesion.

(2.) It was more often a measure of cohesion than of adhesion, a layer of mercury being separated from mercury, or water from water, etc.

(3.) The results obtained as the energy of adhesion were often found to be exactly the opposite to the energy of affinity.

3. Affinity Measured by the Amount of Force required to effect the Decomposition of a Compound.

(α.) *This decomposition may be effected by the agency of heat* (Fourcroy, Lavoisier, etc.).—A very slight heat, for example, is sufficient to destroy the combination of oxygen with certain metals, such as gold or silver, whilst no heat will effect the decomposition of other metallic oxides. Thus it is evident that the force between oxygen and calcium, for example, is very much greater than that between oxygen and gold.

An attempt was made to express this amount in figures; as *e.g.* in the case of the sulphides, by noting the temperatures at which they are decomposed, and deducting therefrom the temperature at which sulphur itself is volatilized. Thus, sulphur volatilizes at 836° F., whilst sulphide of iron (FeS_2) is decomposed at 1500° F. Therefore 1500 — 836 = 674, the amount of the force between sulphur and iron relatively. Sulphide of gold (Au_2S_3) is decomposed at 842° F. 842 — 836 = 6. Therefore, supposing the power of affinity holding the sulphur to the gold to be 6, in the case of iron it is 664; that is, nearly 111 times greater in iron than in gold. Thompson recommends a reverse method of estimating the force, viz., by *a reduction of temperature.* Certain saline solutions part with their salts in the act of freezing, and they do this at various temperatures. Hence, by observing the temperature at which the saturated solution freezes, and remembering that the greater the affinity the lower the temperature, he considered we might be able to form some estimate of its relative force.

(β.) *The decomposition may also be effected by the agency of a superior affinity.*—Mayow in 1674, Geoffrey in 1718, and Bergman in 1775, attempted to estimate the force by what they called *single elective affinity;* that is, where one substance takes away another to the exclusion of a third. Thus, *ammonia* turns out magnesia from magnesic sulphate; *soda,* ammonia from ammonic sulphate; *potash,* soda from sodic sulphate; *strontia,* potash from potassic sulphate; and *baryta,* strontia from strontic sulphate. These experiments led Geoffrey to

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invent tables of attraction, as they were called, such as the following:—

TABLE OF ATTRACTION (Geoffry).

Sulphuric Acid.	*Potash.*
Baryta.	Sulphuric acid.
Strontia.	Nitric acid.
Potash.	Muriatic acid.
Soda.	Acetic acid.
Lime.	Carbonic acid.
Ammonia.	
Magnesia.	

These views held their ground until 1803, when Berthollet pointed out, as the result of a more rigid analysis of the question, the error into which Geoffry and Bergman had fallen, in overlooking the modifying effects of cohesion and elasticity. Further, he showed that Bergman's tables were simply tables of the order of decomposition, and not tables of the attractive force. Berthollet, however, fell into the opposite error of denying the existence of a superior attractive force at all, and of supposing that decompositions were always determined by cohesion and elasticity.

We should note, however, that Bergman was clearly aware of some influence other than affinity, affecting chemical results. This is shown by the fact, that in many cases he compiled two sets of tables, setting forth the different effects resulting from the combination of bodies by solution, and by fusion.

Guyton Morveau, seeing that no dependence could be placed on the measure of chemical action, as deduced from Geoffry and Bergman's tables of "*single elective affinity*," attempted to estimate the force by "*double elective affinity*," that is, where four elements are employed in the decomposition, the two of the one compound reciprocally acting on the two of the other. But still the same modifying influences were at work, and we may conclude with Berthollet that, whilst the tables of affinity give us good ideas of the order of decomposition, they are not, owing to the influence exerted by cohesion and by elasticity, indications of the relative force of affinity.

4. AFFINITY MEASURED BY THE TIME OF COMBINATION.

It was suggested by Wenzel that the time required for one body to dissolve another might serve as a measure of affinity.

Thus he immersed known weights of different metals in a weak acid, and at the end of a given time, estimated the quantity of the several metals dissolved. These quantities he supposed corresponded to the ratio of their affinities.

Again, it will be noted that the energy of the combination will be largely dependent upon the *cohesion* of the body, the temperature of the liquid, and other circumstances.

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5. Affinity measured by Combining Proportions.

When Kirwan was engaged in his inquiries on the composition of salts, he remarked that each salt possessed a different per-centage amount of acid and base, and he supposed that these might serve as a means of estimating the force of affinity. Tables were drawn up by Kirwan as follows:—

Table No. 1.

100 Grains.	Potash.	Soda.	Lime.	Ammonia.	Magnesia.	Alumina.
Sulphuric acid ..	215	165	110	90	80	75
Nitric acid	215	165	96	87	75	65
Muriatic Acid ..	215	158	89	79	71	55

Table No. 2.

100 Grains.	Sulphuric acid.	Nitric acid.	Muriatic acid.
Potash	46·5	46·5	46·5
Soda	60·9	60·9	63·4
Lime	91·0	104·1	112·0
Ammonia	111·1	115·0	126·5
Magnesia	125·0	133·3	141·0
Alumina	133·3	153·6	181·8

Kirwan thus arrived at two general laws:

1. *That the quantity of any base required to saturate a given quantity of any acid, was* DIRECTLY *as the affinities.*—Thus, potash had more affinity for sulphuric acid than soda, soda than lime, lime than ammonia, and so on.

2. *That the quantity of any acid required to saturate any given quantity of a base, was* INVERSELY *as the affinities.*—Thus, sulphuric acid had more affinity for potash than it had for soda, nitric acid less affinity for lime than sulphuric acid, hydrochloric acid less than nitric acid, and so on. Bergman, arguing on the same facts, expressed the law of affinity differently: "*The force of affinity, whether of acid or base, is in the ratio of the quantities required to saturate.*" But it was manifest that this was not so, for the first table would show lime, for example, to have more affinity for sulphuric acid than for nitric acid, whilst the second table would indicate exactly the reverse.

Berthollet again, expressed what he deemed the law of affinity from the same facts as follows: "*The force of affinity is* INVERSELY *as the quantities required to saturate.*"

Again, as Sir H. Davy showed, Berthollet's law involved a contradiction, inasmuch as the action between the constituents of a compound must be mutual. "Sulphuric acid," writes Sir H. Davy, "has as much attraction for baryta as baryta for sulphuric acid. Now baryta is the alkaline earth of which the largest amount is required to saturate

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sulphuric acid, therefore on Berthollet's views it has *the weakest affinity* for that acid. But less sulphuric acid saturates baryta than any other earthy or alkaline body, therefore, according to Berthollet, sulphuric acid has *a stronger affinity* for baryta than for any other substance, which is contradictory."

Again, experiment proves Berthollet's law fallacious. From his tables, such as the following, it would seem that ammonia had a greater affinity for sulphuric acid than baryta, and carbonic acid a greater affinity for baryta than sulphuric acid, which we know not to be the case;—

40 parts of Sulphuric acid require for neutralization.	77 parts of Baryta require for neutralization.
292 Morphia.	165 Iodic acid.
162 Quinine.	118 Bromic acid.
77 Baryta.	76 Chloric acid.
52 Strontia.	54 Nitric acid.
48 Potash.	49 Sulphuric acid.
32 Soda.	37 Muriatic acid.
28 Lime.	36 Oxalic acid.
20 Magnesia.	22 Carbonic acid.
17 Ammonia.	

Berthollet, however, was fully aware of the contradictory results of the law and of experiment, but explained these contradictions by reference to the effects of cohesion and elasticity.

It is certain, however, that combining proportions and power of saturation, are in no respect a measure of relative affinity.

6. Affinity measured by the Electrical Condition.

Thompson has drawn up a table of affinity, founded upon the order of decomposition, as effected by electrical influence.

Becquerel points out that if a current of electricity of known activity be passed through a mixed solution of the metals, it decomposes them in a given order. If a solution, for example, be made, containing *atomic proportions* of argentic nitrate, cupric nitrate, and plumbic nitrate, and a galvanic current be passed through the liquid, the silver will be thrown down first, then the copper, and finally the lead. Thus it would seem that the silver had the least affinity for oxygen, and lead the most. But if, instead of mixing these nitrates in atomic proportions, a greater quantity than its equivalent of cupric nitrate be added, there comes a time when both copper and silver will be thrown down together, mass thereby overcoming resistance. It is an important question yet to be decided, whether the order and the rate of decomposition of a mixed solution of metallic salts in atomic proportions, coincide with the results obtained by experimenting on solutions where the resistance is overcome by quantity.

Summarizing these facts we may note, first, that we have no means of estimating the force of affinity *absolutely;* and secondly, but very uncertain means of estimating it *relatively.*

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CHAPTER II.

Nomenclature—Chemical Symbols and Formulæ—Combining Proportions—Atoms—Molecules—Atomic and Molecular Combination—Compound Radicals—Volume—Standard Pressure and Temperature—Relative Weight—The Crith—Relation between Atomic Weights and Specific Gravity—Relation between Atomic Weights and Specific Heats—Atomicity and Quantivalence—Chemical Formulæ—Substitution—Isomerism—Isomorphism—Allotropism—The Metric System.

Elements and Compounds.—By an element or *simple* body we understand a substance which cannot be decomposed, and from which nothing can be taken but the substance itself. Iron is an element; you can extract nothing from iron but iron. The elements are divided into two classes—metals and non-metals, or metalloids. This division, however, is arbitrary.

By a *compound* body we understand one formed by the union of two or more elementary bodies. Common salt is a compound body. It may be formed by combining sodium and chlorine. From common salt we can obtain sodium and chlorine. The first is the *synthetical* proof, and the second the *analytical* proof, of its compound nature.

Names of Bodies.—The ancient names given to bodies were most often fanciful. They were derived either (α) *from their resemblance to certain things* (as, *e. g.*, oil of vitriol, sugar of lead, butter of antimony liver of sulphur, etc.); or (β) *from some remarkable property of the body* (as, *e. g.*, caustic alkali, corrosive sublimate, vital air, sal polychrest, phosphorus, antimony, etc.), or (γ), *from the names of a person or heathen divinity*, (as *e. g.*, Glauber's Salts, Tantalum, Niobium, etc.) or (δ) *from the name of a place* (as, *e. g.*, Epsom salts, Cheltenham salts, Columbium, etc.), or (ε) *from the name of a planetary body* (as, *e. g.*, Tellurium, Uranium, etc.)

A reformation in nomenclature was suggested, in 1781, by Guyton Morveau, who proposed that the name should indicate somewhat the properties and composition of the body, and should have its root in the dead languages. In 1787, he obtained for this purpose the assistance of the French Academy of Sciences, and Lavoisier, Berthollet, and Fourcroy were appointed to join him in the work. To a large extent their efforts were successful.

Many of the names of bodies now employed, express some special characteristic. Thus chlorine (χλωρὸς, green) refers to the color of the substance; bromine (βρῶμος, stench) to its odor, etc. Most of the metals, although many of the common names are retained, are distinguished by the termination *um*. The haloid group terminate in *ine*; some terminate in *on*, as carbon and boron; and some in *gen*

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(γεννάω), as hydrogen (water-begetter), oxygen (acid-begetter), nitrogen (nitro-begetter), etc.

In the case of compounds, the name is made to express *the components* of the body, and, as far as possible, *its constitution.* Thus, the name "sodic chloride" expresses a compound of sodium and chlorine. The term "*anhydride*" signifies a binary compound containing oxygen (an oxide), which, when combined with water, forms an acid; for example—

$$SO_3 + H_2O = H_2SO_4.$$
Sulphuric anhydride + Water = Sulphuric acid.

We may here consider the meaning of the various terminations and prefixes used in chemical nomenclature.

I. Terminations.

(1.) "*ide*" is applied to the negative constituent of a binary compound (that is, a compound formed by the union of two elementary bodies), the positive constituent being made to terminate in "ic." For example—

Potassium + Iodine form Potassic Iod*ide*.
Lead + Oxygen ,, Plumbic Ox*ide*.

[Note.—Sir H. Davy suggested that the terminations in these cases should indicate property, "*ide*" being employed for acid, and "*uret*" for alkaline compounds.]

(2.) "*ic*" and "*ous*."—Two bodies may combine in different proportions. Thus, tin and chlorine combine to form $SnCl_2$ and $SnCl_4$. The termination *ic* is given to the *positive* constituent of the compound (Sn) which contains the *largest* proportion of the *negative* constituent (Cl), and the termination *ous* to the *positive* constituent, which contains the *smallest* proportion of the *negative* constituent. For example—

$$Sn + Cl_2 = SnCl_2.$$
1 Tin + 2 Chlorine = Stann*ous* chloride.

$$Sn + Cl_4 = SnCl_4.$$
1 Tin + 4 Chlorine = Stann*ic* chloride.

(Similarly FeO = ferr*ous* oxide, Fe_2O_3 = ferr*ic* oxide; Hg_2O = mercur*ous* oxide, HgO = mercur*ic* oxide; etc.)

These terminations "*ic*" and "*ous*," moreover, are employed to distinguish acids that are composed of the same elements, but in different proportions. Thus, sulphur forms two acids by its combination with oxygen. The acid which contains the most oxygen is called sulphur*ic* acid, whilst that containing the least oxygen is called sulphur*ous* acid.

Sulphur*ous* acid Phosphor*ous* acid Nitr*ous* acid	Contain less oxygen than	Sulphur*ic* acid. Phospor*ic* acid. Nitr*ic* acid.

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(3.) "*ite*" and "*ate*."—The termination "*ite*" implies that the salt is a compound of a base and an acid terminating in "*ous*," and the termination "*ate*" that the salt is a compound of a base and an acid terminating in "*ic*;" for example—

Sodic sulph*ite* is a salt of Sulphur*ous* acid.
Sodic sulph*ate* „ Sulphur*ic* acid.

(4.) "*a*" and "*ia*."—The termination "*a*" is usually given to inorganic alkalies," such as soda, and "*ia*" to organic alkalies, such as strychnia. The rule is not absolute.

(5.) "*ine*" or "*in*" are used to denote a neutral alkaloid, such as caffeine, piperin, etc.

(6.) "*yl*" or "*yle*" is adopted in the case of many of the compound radicals, such as methyle, propyl, etc. In these latter cases the rule is by no means constant.

II. Prefixes.

(1.) *Bin*, *Ter*, etc. (Latin); or *Mon* or *Mono*, *Deut*, etc. (Greek); or *Di*, *Tri*, *Tetra*, etc., denote various proportions of constituents, and the position of various compounds in a series; for example—

Carbonic monoxide (or oxide) signifies C + O.
Carbonic dioxide (or anhydride) „ C + O_2.

There is no rule as to the use of the Latin or the Greek forms.

(2.) "*Per*" denotes the highest compound in a series; for example, a *peroxide* signifies that oxide which contains the largest quantity of oxygen in a series of oxides.

(3.) "*Sesqui*" denotes a compound where the relationship of the elementary atoms is as 2 to 3; for example, sesquioxide of iron (really ferric oxide) has the formula Fe_2O_3.

(4.) "*Proto*" (πρῶτος, first) denotes the first of a series of compounds; for example, the protoxide of iron FeO (also called ferr*ous* oxide) contains the smallest quantity of oxygen of any iron and oxygen compound.

(5.) "*Hypo*" (ὑπὸ, under) denotes the position of a compound. Thus, the acid containing *less* oxygen than *sulphurous acid*, is called *hyposulphurous* acid.

(6.) "*Hyper*" (ὑπὲρ, over) refers to the converse of the prefix "hypo." Thus, *hyper*sulphur*ous* acid (commonly called *hypo*sulphur*ic* acid) denotes an acid containing *more* oxygen than *sulphurous acid*.

(7.) "*Para*" signifies equal; for example, *para*cyanogen implies a body chemically equal to cyanogen.

(8.) "*Meta*" signifies "near to." Thus, *meta*phosphoric acid only differs from orthophosphoric acid by 1 molecule of water.

(9.) "*Sub*" implies that the compound contains less of a constituent than is indicated by the rest of the word.

(10.) "*Sulph*" or "*Sulpho*," "*Hydr*" or "*Hydro*."—The composition of acids formed by the combination of sulphur or hydrogen (*without*

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oxygen) with other elements is expressed by the foregoing prefixes, the terminals "*ous*" and "*ic*" being also employed, in the case of the sulphur compounds, to indicate the proportions of sulphur relatively present. In the case of hydrogen, such terminations are not needed, inasmuch as only one acid is formed by the union of an element with hydrogen.

Chemical Symbols and Formulæ.

The alchymists adopted signs to represent bodies. Thus ☉ (sol) represented gold, and ☽ (luna) silver, etc. Chemists now-a-days denote the various elementary bodies by symbols, using either the first letter of the Latin name, or, where several elements have the same initial letter, the first letter conjoined with a smaller one. Thus, O = oxygen; C = carbon; Ca = calcium; Cl = chlorine, etc.

Further, this symbol represents one equivalent or combining weight of the element. Thus, the symbol O represents *a similar bulk* of oxygen, that the symbol H represents of hydrogen, but *a weight* 16 times as great.

A compound is represented by the symbols of the several components placed one after the other. Thus, HCl represents a compound, formed of one atom of hydrogen and one of chlorine, or by 1 part by weight of hydrogen and 35·5 parts by weight of chlorine.

If we desire to express more than one atomic proportion, we place a little figure above or below the symbol. Thus, H_2O (or H^2O) implies that with every atom or 1 atomic part by weight of oxygen there is conjoined 2 atoms or 2 atomic parts by weight of hydrogen.

If the figure be placed before the whole formula, it implies that all the elements composing the group, *i. e.*, either as far as a comma, or some other sign following, or else included in brackets immediately succeeding the number, are to be multiplied by the said number. Thus, in the equation* $Ca_3P_2O_8 + 2(H_2SO_4) = 2(CaSO_4) + H_4CaP_2O_8$, the 2 before the H_2SO_4 and the 2 before the $CaSO_4$ implies that the whole number is to be multiplied by 2; but there being a + after the $CaSO_4$, it follows that the $H_4CaP_2O_8$ is *not* to be multiplied by the 2 preceding the $CaSO_4$.

It is not, however, necessary to employ brackets unless a comma be introduced into the formula; thus, in the equation—

$$Ca_3P_2O_8 + 2H_2SO_4 = 2CaSO_4 + H_4CaP_2O_8$$

the multiplication of the H_2SO_4 and of the $CaSO_4$ respectively by 2 is just as much indicated, as if the formulæ had been placed within brackets. Thus, the formula $3Cu,2NO_3$ implies that the Cu only is to be multiplied by 3, and not the $2NO_3$; whilst if the formula fol-

* A chemical "*equation*" signifies the expression of chemical reactions by chemical formulæ.

It will be remarked that in chemical as in algebraical equations, the sign + signifies addition (or admixture); the sign — subtraction, and the sign = equals (or yields, or is converted into).

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lowing the number be placed in brackets, thus, $3(Cu,2NO_3)$, it then implies that the whole number is to be multiplied by 3. Thus—

$3Cu,2NO_3$ would be equivalent to $Cu_3N_2O_6$; but

$3Cu2NO_3$ or $3(Cu,2NO_3)$ " " $Cu_3N_6O_{18}$.

Combining Proportions—Atomic Theory.

In 1774, Wenzel, a German chemist, published a work on "The General Theory of Affinities." This in reality, contained the germ of the atomic theory. The great fact noted by Wenzel was, that when two neutral salts, such as sodic sulphate, and plumbic acetate were mixed together, an exchange of acids took place, but that, nevertheless, the resulting products were neutral, proving, as he remarked, that the acid of the one salt was sufficient for the base of the other salt.

In 1792 Richter, a Prussian chemist, wrote a work on "Stochiometry, or the Mathematics of Chemical Elements" (στοιχεῖον, an element, μετρέω, I measure). This was mainly directed to illustrating the relative quantities of acid and base necessary for saturation. He further constructed numerous tables, such as the following, as the result of his enquiries* :—

1. *Acids.*

Fluoric	427
Carbonic	577
Sebacic	706
Muriatic	712
Oxalic	755
Phosphoric	979
Formic	988
Sulphuric	1000
Succinic	1209
Nitric	1405
Acetic	1480
Citric	1683
Tartaric	1694

2. *Bases.*

Alumina	525
Magnesia	615
Ammonia	672
Lime	793
Soda	859
Strontia	1329
Potash	1605
Barytes	2222

In 1800, whilst Dalton was analysing some compounds of hydrogen and carbon, he remarked that the several quantities advanced in multiple proportions. The same, moreover, he found to be true with other compounds, such as those of carbon and oxygen, sulphur and oxygen, etc. It therefore occurred to him "*that matter was composed of particles of definite weights, and that it combined in those weights.*

This constituted Dalton's "Atomic Theory," the fundamental propositions of which were—

(1.) That matter is composed of indivisible and indestructible particles called *atoms.*

(2.) That the atoms in a mass do not touch, but are surrounded by an atmosphere of heat.

* These tables are taken from Thompson, and represent the mutual combining proportions of acid and base.

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(3.) That they are endowed with attractive and repulsive forces.

(4.) That they have specific weights.

Atoms (*a, not,* and *τέμνω, I cut*).—Here we refer entirely to the atoms of elementary bodies and not to "*compound radicals,*" which have been called "*compound atoms.*"

(1.) Every element consists of ultimate particles called "*atoms.*" The chemical symbol of any element represents this atom. Thus, O represents the atom or smallest indivisible particle of oxygen.

(2.) We have no actual knowledge either of *the shape,* or of the *absolute weight,* or of the *absolute volume* of these atoms.

(3.) The atoms of any given substance are believed to be of identical weight, under any and every condition. One atom of oxygen weighs the same as every other atom of oxygen;—

(4.) Nevertheless the atom of one body does not weigh the same as the atom of every other body. An atom of oxygen weighs 16 times as much as, and an atom of carbon 12 times as much as, an atom of hydrogen. These *comparison weights* of the atoms, (hydrogen as the lightest body known, being regarded as 1,) are called *atomic weights.* Atomic weights, therefore are *relative weights,* but not *absolute weights.* For example: When we say that mercury has an atomic weight of 200, we mean, that the atom of mercury would weigh 200 times as much as the atom of hydrogen, but inasmuch as we cannot determine the absolute weight of the hydrogen atom, the number 200 does not express the absolute weight of the mercury atom.

Accurately, we may define the *atomic weight* of an element, as "*that weight which would occupy in the state of gas the same volume as the unit weight of hydrogen under the same temperature and pressure.*"

If, however, we cannot obtain the element in a state of gas (as, *e. g.,* in the case of carbon), the atomic weight is then deduced from other considerations such as the specific heat of the body, etc.

By the term "*combining proportion*" Sir H. Davy implied the smallest proportion *by weight* (hydrogen being regarded as unity), in which bodies combine with each other.

Molecule (*Molecula, a little mass.*)—These may be compound or elementary.

(a.) *Compound Molecules.* A compound body is made up of two or more elementary atoms. A molecule of any given compound is "*the smallest possible cluster of elementary atoms capable of existing as the compound, and of having an independent chemical action.*" Thus a molecule of water (H_2O) consists of 2 hydrogen atoms and 1 oxygen atom. Therefore the water molecule consists of 3 atoms, inasmuch as nothing less than an aggregate of 3 atoms can form water. Or again, a molecule of ammonia (NH_3), consists of 4 atoms, viz., 3 of hydrogen and 1 of nitrogen. It could not be ammonia if there were less than 4 atoms present. *A molecule, therefore, may be a cluster of any number of atoms from two upwards.*

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The atomic weight of a molecule is the sum of the weights of the several atoms of which it is composed. Thus 18 is the atomic weight of a molecule of water ($H_2O=2+16$). The molecular weight of a hydrogen salt is always that weight which contains as many hydrogen atoms as can be replaced by potassium, silver, etc. Thus $C_2O_4H_2$ is the formula for a molecule of oxalic acid, and 90 is its molecular weight. We do not regard CO_2H as its formula, or 45 as its molecular weight, because we are able, not only to replace both atoms of hydrogen by potassium, forming the *neutral potassic oxalate* $C_2O_4K_2$, but to replace one hydrogen atom only by potassium, thereby forming *hydric potassic oxalate* C_2O_4HK.

Conversely, we represent 63 as the molecular weight of HNO_3, and not 126 (viz., $H_2N_2O_6$) because, whilst we have the salt KNO_3 we know of no such salt as HKN_2O_6.

(*b.*) *Elementary molecules.*—There are strong reasons for believing that our knowledge of the reactions of elements pertains exclusively to their *molecular* and not to their *atomic* condition, and that in all decompositions and combinations the molecule of the element is concerned, although only one of the atoms of the molecule may be at work in effecting the change. Hence a free element, such as hydrogen, never appears to work singly, but in clusters, and we therefore, in a molecular formula, double the simple or atomic formula. In a bottle of hydrogen therefore, we shall do well to regard the gas, not as made up of particles of $\boxed{\text{H}} = 1$, but as made up of atom-clusters of $\boxed{\begin{array}{|c|c|}\hline \text{H} & \text{H} \\ \hline \end{array}} = 2$; and the convenience of this diatomic symbolization, as it is called, will appear further, when we note that, with very few exceptions, compound bodies in their vaporous condition, occupy two volumes. This leads us to define—

An atom of an elementary body as the smallest proportional weight of that body capable of existing in chemical combination; and

A molecule of an elementary body as the smallest proportional weight capable of existing in a free or uncombined state.

By the phrase *molecular weight*, then, we imply "the weight of *two* volumes of any substance, elementary or compound, compared with the weight of two volumes of hydrogen." Thus—

$H_2=2$: Therefore the molecular weight of $O_2=32$, of $Cl_2=71$, of $HCl=36{\cdot}5$.

The symbol of a compound body represents a molecule of that body.

Dr. Frankland expresses this fact by stating that no element can exist with any of its bonds unconnected, and that therefore the molecules of all elements having an uneven number of bonds are generally diatomic, but are always polyatomic. Thus—

Hydrogen (H'_2) H—H; *Nitrogen* (N^{v}_{2}) N $\equiv$ N; *Phosphorus* (P^{v}_{4}) $\begin{array}{ccc} \text{P} & = & \text{P} \\ \| & & \| \\ \text{P} & = & \text{P} \end{array}$

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In some cases (viz., mercury, zinc, and cadmium) we find an element capable of existing as a monatomic molecule, its own bonds satisfying each other. In such a case, however, its atomicity must be even (artiad). Thus—

Mercury (Hg″) —Hg—; *Zinc* (Zn″) —Zn—; *Cadmium* (Cd″) —Cd—;

but, on the other hand, such an element may be also polyatomic, as in ozone, which is an allotropic form of oxygen where the molecule is triatomic. Thus O_2 (O=O) represents the ordinary diatomic molecular form of oxygen, whilst O_3 $\left(\begin{array}{c} O \\ \diagup\diagdown \\ O—O \end{array}\right)$ represents the triatomic molecule of ozone.

Combination by Weight.

The laws of chemical combination as taught by Dalton are as follows:—

I. *That every definite chemical compound has a fixed and invariable composition; that is, a given compound always consists of the same elements united in the same proportions.*

Thus, hydrochloric acid (HCl) consists of 1 atom of hydrogen (H) combined with 1 atom of chlorine (Cl). The weight of the hydrogen atom being 1, and the chlorine atom 35·5, it follows that in every 36·5 grains, or pounds, or tons of hydrochloric acid, there is 1 grain, or pound, or ton of hydrogen, and 35·5 grains, or pounds, or tons of chlorine. Hydrochloric acid can be formed in no other proportion than 1 part of hydrogen to 35·5 parts of chlorine.

II. *If one substance combines with another in more than one proportion, the several proportions are always some multiple or sub-multiple of the lowest of these proportions.*

This is illustrated, for example, in the oxides of nitrogen:—

		Nitrogen.	Atomic weight of Oxygen.
Nitrous oxide	N_2O	28	to 16.
Nitric oxide	N_2O_2	28	to 16 × 2 = 32.
Nitrous anhydride	N_2O_3	28	to 16 × 3 = 48.
Nitric peroxide	N_2O_4	28	to 16 × 4 = 64.
Nitric anhydride	N_2O_5	28	to 16 × 5 = 80.

It will be seen how the various quantities of oxygen increase by definite multiples of 16. It often happens, however, that a series may be deficient, or that the proportions are less simple than in the illustration given.

III. *If the weights in which a series of bodies* (B, C, D, E, etc.) *combine with another body* (A) *be determined, these weights or some multiple or sub-multiple thereof, are also the weights with which* B, C, D, *and* E *combine amongst themselves:—*

Example: 16 of oxygen will combine with 65 of zinc, and
16 × 2 = 32 of oxygen ,, 32 of sulphur;
Therefore 65 of zinc ,, 32 of sulphur.

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IV. *In a compound body, the combining weight of the compound is the total combining weight of the components.*

For example, the combining weight of sulphur is 32, and of oxygen 16. The combining weight of sulphuric anhydride (SO_3), which is composed of 1 of sulphur and 3 of oxygen is, therefore, 80.

These facts give accuracy to all chemical reactions. In the laboratory no materials are mixed at random; bodies combine in exact proportions, and form products of definite weights. It follows that, "*As the total molecular weight of the substance given is to the total molecular weight of the substance required, so is the given weight to the required weight.*" That is, if we desire to obtain 500 grammes of carbonic anhydride from sodic carbonate, knowing that every 106 parts of sodic carbonate contain 44 parts of carbonic anhydride, the exact quantity of sodic carbonate necessary to produce the 500 grammes may be estimated by the equation—

$$44 : 106 : : 500 : x.$$

Atomic and Molecular Combination.—H represents an atom of hydrogen. H_2 represents a molecule of hydrogen, or the smallest portion of hydrogen capable of existing in the free state. Cl similarly represents an atom, and Cl_2 a molecule of chlorine. To express the combination of these bodies in *atomic formula* we write it thus—

$$Cl + H = HCl,$$

whilst to express their combination in *molecular formula* we write it thus—

$$Cl_2 + H_2 = 2HCl.$$

this latter implying the bringing together of two molecules, and a mutual interchange occurring, whereby two molecules of a new body are formed. Two molecules occasionally, though rarely, unite to form one molecule, from the latent atomicity of an element becoming active. Thus—

$$''\mathbf{C}''O + Cl_2 = \mathbf{C}^{iv}OCl_2 \ (\textit{phosgene gas}),$$

where the *latent* atomicity of the carbon equal to 2 in the **C**O becomes *active* in the **C**OCl_2, thereby making the active atomicity of the carbon in the latter compound, double what it was in the former.

There is what Frankland calls a *molecular union* or *combination*, where no change results in the active atomicities; as, for example, in the combination of salts with their water of crystallization. In such cases we place a comma between the molecules. Thus, crystallized magnesic sulphate is represented by Frankland as **S**$OHo_2Mg o'',6\mathbf{O}H_2$, which implies that the $6\mathbf{O}H_2$ is molecularly combined with the salt. Such combinations are, for the most part, unstable.

Compound Radicals.—A compound radical is "*a group of two or more atoms, which behaves in all respects as though it were an element.*"

Such compound groupings were supposed by Liebig to be peculiar

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to bodies of organic origin, but their existence is now recognised amongst inorganic substances.

Theoretically, the number of compound radicals must be endless; practically, however, chemists only dignify those groupings as compound radicals, that can be shown to enter into the composition of a large number of compounds.

Respecting these compound radicals we must note that—

(1.) Every compound radical must contain a polyad element; that is, an element requiring two or more hydrogen atoms, or their equivalent, to saturate it.

(2.) Compound radicals, like the elements, are of different atomicities, the atomicity depending on the number of hydrogen or other monad atoms required to satisfy them. Thus—

If you remove H from the fully saturated NH_3 (ammonia), a "residue" or "compound radical" remains, which is no longer saturated, called amidogen (NH_2) of *monad* atomicity. Thus, amidogen will combine with the monad element potassium, to form potass-amine (NH_2K).

If you remove H_2 from NH_3, a radical is left called imidogen (NH), of *dyad* atomicity. Thus, imidogen will combine with two atoms of the monad compound radical methyl (CH_3) to form dimethyl-amine $NH(CH_3)_2$.

(3.) The molecule of a monad, triad, or pentad compound radical, like the atom of a monad, triad, or pentad element, cannot exist in a free state, but when isolated combines with itself. Thus, H_2 represents a molecule of hydrogen, and $(HO)_2$ a molecule of the monad compound radical hydroxyl.

A few examples will render these facts clear, and illustrate their application.

In *nitric acid* we have a body built up on the water type, containing a *monad* compound radical NO_2 in the place of a hydrogen atom.

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O = H_2O\,[\mathbf{O}H_2];\ \text{so}\ \left.\begin{matrix}NO_2\\H\end{matrix}\right\}O = HNO_3\,[\mathbf{N}O_2Ho.]$$

In *sulphuric acid* we have the *dyad* compound radical SO_2 having *two* unsatisfied bonds (—O—S—O—), each bond being combined with (Ho); thus—

$$SO_2\left\{\begin{matrix}HO\\HO\end{matrix}\right.\ \text{or}\ H_2SO_4 = [\mathbf{S}O_2Ho_2.]$$

In *phosphoric acid* we have the *triad* compound radical (PO) having *three* unsatisfied bonds, phosphorus being a pentad, each bond being combined with (Ho); thus—

$$PO\left\{\begin{matrix}HO\\HO\\HO\end{matrix}\right. = H_3PO_4\,[\mathbf{P}OHo_3.]$$

In *organic* chemistry we have the well-marked compound monatomic radical, cyanogen (CN or Cy). Like chlorine, which combines

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with hydrogen to form hydrochloric acid (HCl), it combines with hydrogen to form hydrocyanic acid (HCy), two volumes, as in the former case, combining without condensation.

Dr. Frankland recognizes in his notation the following compound radicals:—

	Molecular formula.	Semi-molecular formula.	Semi-molecular symbols.
Hydroxyl	$(HO)_2$ ...	... HO ..	... Ho
Hydrosulphyl ...	$(HS)_2$ ...	... HS ...	... Hs
Ammonium	$(NH_4)_2$ ...	... NH_4...	... Am
Ammonoxyl... ...	$(NH_4O)_2$	... NH_4O	... Amo
Amidogen	$(NH_2)_2$ ...	... NH_2...	... Ad

Compounds of metals with oxygen, each oxygen atom being combined with the metal by one bond only, the other or others being free to combine with other elements, are also regarded as compound radicals.

	Molecular formula.	Semi-molecular or combining symbols.	Graphic formula.
Potass-oxyl ...	$(KO)_2$	... Ko ...	—O—K
Zinc-oxyl ...	(ZnO_2)	... Zno″ ...	—O—Zn—O—

In adopting the abbreviated form for the compound radical (*e.g.*, Ko, Zno″) the use of the little o merely expresses that it forms part of the radical, but it does not express the atomic proportion in which the oxygen is present, this being determined by the atomicity of the element with which it is associated, and which, as in the case of the elements, is marked by dashes.

Thus: Ko=KO; Zno″=ZnO_2.

Volume (*volvo*, I roll).—"A volume" in chemical language implies the space occupied by a known weight of a gas at a given temperature and pressure, compared with the space occupied by known weights of other gases at a similar temperature and pressure.

Gay Lussac in 1809 proved that, as in compound bodies the elementary atoms combine in fixed weights (as shown by Dalton), so, in gaseous compounds, the constituents combine in fixed volumes.

The symbols H, O, Cl represent atoms of hydrogen, oxygen, and chlorine, having relative weights of 1, 16, and 35·5 respectively. If we take 1 gramme of hydrogen we should find that at a certain temperature and pressure the volume of the gas would measure 11·2 litres. In order to obtain a volume of oxygen measuring 11·2 litres, or a volume of chlorine measuring 11·2 litres at a similar temperature and pressure, we should require in the former case 16 grammes, and in the latter case 35·5 grammes. These weights are, it will be noticed, the atomic weights of oxygen and chlorine. *Hence, the symbols* H, O, *and* Cl *represent different weights of the gases, but similar bulks.*

Again, imagine this ⌷ to represent separate volumes of hydrogen, oxygen, and chlorine. If this volume of hydrogen weighed 1

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grain, a similar volume of oxygen would weigh 16 grains, and of chlorine would weigh 35·5 grains. *Hence the symbols* H, O, Cl *represent similar bulks of the several gases, but different weights.*

These facts were first noted in 1811 by Amedeo Avogadro, and in 1814 by Ampère. They remarked that the effect of changes of temperature and pressure on all gases was alike, and reasoning on the constancy of the results they concluded "*that equal volumes of all substances in a gaseous state contain under like conditions the same number of molecules*" ("Journal de Physique," July, 1811). But, inasmuch as equal volumes had different weights, it followed that the molecules of different gases must also have different weights.

An illustration will make these facts clear:—

(*α.*) The volume-combination of hydrogen and chlorine to form hydrochloric acid may be thus expressed,

$$\boxed{\text{H}} + \boxed{\text{Cl}} = \boxed{\text{H}|\text{Cl}};$$

which implies that a given volume of hydrogen combines with a similar volume of chlorine to form two volumes of hydrochloric acid.

(*β.*) The combination of hydrogen and chlorine by weight is expressed thus—

$$\text{H} + \text{Cl} = \text{HCl};$$

which implies that 1 part by weight of hydrogen combines with 35·5 parts by weight of chlorine to form 36·5 parts by weight of hydrochloric acid.

(*γ.*) If therefore the hydrogen volume has a weight of 1, the chlorine volume must have a weight 35·5 times as great; inasmuch, however, as both volumes contain the same number of molecules, it follows that the weight of the chlorine molecule must be 35·5 times that of the hydrogen molecule.

(*δ.*) It is evident that the volume of any two gases making a compound are to one another as the atoms of the elements forming the compounds. Thus—

$\text{H} + \text{Cl} = \text{HCl}$; *i.e.* { 1 atom of H combines with 1 atom of Cl, or 1 vol. of H combines with 1 vol. of Cl.

$\text{H}_2 + \text{O} = \text{H}_2\text{O}$; *i.e.* { 2 atoms of H combine with 1 atom of O, or 2 vols. of H combine with 1 vol. of O.

(*ε.*) To this law there are certain exceptions:—

(1.) In the case of *Phosphorus* and *Arsenic*, the *number of volumes must be halved,*

Thus—

In PH_3, { 3 vols. of H combine with $\frac{1}{2}$ vol. of P vapour; or 6 vols. of H combine with 1 vol. of P vapour.

In AsH_3, { 3 vols. of H combine with $\frac{1}{2}$ vol. of As vapour; or 6 vols. of H combine with 1 vol. of As vapour.

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(2.) In the case of *Mercury, Zinc, and Cadmium*, the number of volumes must be doubled.

Hence, the general facts may be stated as follows:—"The combining volumes of all elementary gases are equal, excepting Phosphorus and Arsenic, which are *one-half*, and Zinc, Mercury, and Cadmium, which are *double* those of the other elements in the gaseous state."

Standard Pressure and Temperature.

In connection with our study of volume-combination, it is important to understand the method of correcting gases to standard temperature and pressure, when the volume is estimated at irregular temperatures and pressures.

The standard pressure is when the barometer stands at 30 inches or 760 millimètres (really 29·92 inches), and *the standard temperature* is regarded as 0° Centigrade.

(1.)—**Standard Pressure.**—This implies "*the pressure of a column of mercury of* 30 *inches, or of* 760 *mm, at the temperature of* 0° *C.*"

By the term "1 pressure" or "1 atmosphere" is implied the weight of a 30-inch column of mercury, which the air (on an average) is capable of supporting. Such a column is found to press with a weight of 15 lbs. on the square inch. A pressure of 15 lbs. on the square inch, therefore, constitutes what is called "1 pressure" or "1 atmosphere;" a pressure of 30 lbs. on the square inch constituting "2 pressures" or "2 atmospheres," etc.

The relationship of the volume of a gas to pressure, known as the Law of Boyle and Marriotte (1662) is as follows:—"*The temperature being constant, the volume of a gas varies inversely as the pressure;*" that is, the smaller the pressure, the greater the volume; the greater the pressure, the smaller the volume.

A given quantity of any gas at	1 pressure	=	1 volume.
,,	,,	2 pressures	= $\frac{1}{2}$ volume.
,,	,,	4 pressures	= $\frac{1}{4}$ volume.
,,	,,	$\frac{1}{2}$ pressure	= 2 volumes.
,,	,,	$\frac{1}{4}$ pressure	= 4 volumes.

Or the facts may be stated thus:—

1 litre of gas at 30 in. B.P. (760 mm.), would occupy 2 litres at 15 in. B.P. (380 mm.), and 0·5 litre at 60 in. B.P. (1,520 mm.); or 100 cubic inches at 1 pressure would become 50 cubic inches under a pressure of 2 atmospheres, and 200 cubic inches under a pressure of half an atmosphere.

To correct a gas, therefore, from an irregular pressure to the standard pressure, the simple rule is,—

As the required pressure (*i.e.* 30 in. or 760 mm.) *is to the given pressure, so is the given bulk to the required bulk.*

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Examples—

(α.) If a gas occupies 250 cubic in. at 29·2 in. B.P., what bulk will it occupy at standard pressure?

30 : 29·2 :: 250 : x. *Ans.* 243·3 c. i.

(β.) If at 754 mm. a gas measures 1·25 litres, what will it measure at standard temperature?

760 : 754 :: 1·25 : x. *Ans.* 1·240 litre.

(γ.) What bulk will a gas occupy at 29 in. B.P. which measures 0·6 litre at 30 in.?

29 : 30 :: 0·6 : x. *Ans.* 0·62 litre.

(2.)—**Standard Temperature.**—The law of Charles states that "*The volume of a given mass of gas, the pressure being constant, varies directly as the absolute temperature.*"

The standard of temperature is regarded as 0° C.

The law of Charles therefore declares, that gases, unlike solids and liquids, expand by heat and contract by cold *regularly* for every increase or decrease of temperature. *What, then, is this regular increase?* Experiment proves that it is an increase of the $\frac{1}{273}$ part of the volume of the gas (or 0·00366), for every 1° C., or the $\frac{1}{490}$ part (or 0·00204) for every 1° Fah.; Hence—

273 vols. at 0° C. become 274 vols. at 1° C.
273 ,, ,, 275 ,, 2° C.
273 ,, ,, 373 ,, 100° C.

If, therefore, a gas measures a litre at 273° C., it will only measure half a litre at 0° C., the pressure being constant.

To correct for temperature, the rule is,—

"*As* 273 + *the given temperature* (*in Centigrade degrees*) *is to* 273 + *the required temperature, so is the given bulk to the required bulk.*"

Examples—

(α.) A gas measures 1 litre at 273·0° C., what will it measure at 0° C. (standard temperature)?

273 + 273 : 273 + 0 :: 1 : x. *Ans.* x = 0·5 litre.

(β.) A gas measures 25 cubic in. at 20° C., what will it measure at the standard temperature?

273 + 20 : 273 + 0 :: 25 : x. *Ans.* x = 23·29 c. i.

In stating, therefore, the volume of a gas, it must in all cases be corrected, (1) *to standard pressure* (30 in. or 760 mm.), the bulk of the gas varying, according to the law of Marriotte, "*inversely as the pressure;*" and (2) *to standard temperature* (0° C.), the bulk of the gas varying, according to the law of Charles, "*directly as the temperature.*"

Molecular Combination. Combination by Volume. Doctrine of Types.

(1.) *A molecule of hydrogen* $\left.\begin{matrix}H\\H\end{matrix}\right\}$ is represented thus $\boxed{H|H}$ (*Hydrogen Type*).

One of the H atoms of the molecule, may be replaced by one or other of the haloid elements (Cl, Br, I, F), to form a hydracid; Thus—

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$$\boxed{H} + \boxed{Cl} = \boxed{H\,Cl} \text{ or } 1 + 35{\cdot}5 = 36{\cdot}5.$$
1 vol. + 1 vol. = 2 vols.

Such acid may be represented as the combination of 2 volumes of chlorine (1 molecule) with 2 volumes (1 molecule) of hydrogen, four volumes of hydrochloric acid gas resulting.

$$\boxed{H\,H} + \boxed{Cl\,Cl} = \boxed{\begin{array}{c|c} HCl & HCl \\ \hline HCl & HCl \end{array}}$$

Whenever 1 *volume of one gas combines with* 1 *volume of a second gas, no condensation results; that is, the bulk of the compound formed, is the same as the bulk of the two gases, and the weight as the weight of the two gases, from which it was produced.* The fact, therefore, is that—

1 *litre of chlorine* + 1 *litre of hydrogen* = 2 *litres of hydrochloric acid gas.*

Or, in other words, a given bulk of hydrochloric acid gas is one-half hydrogen and one-half chlorine. The same is also true of hydriodic acid, hydrobromic acid, &c., which are also formed on the hydrogen type.

(2.) $\left.\begin{matrix} H \\ H \end{matrix}\right\}$ O represents *a molecule of water* (*Water Type*).

Whenever 2 *volumes of one gas combine with* 1 *volume of another gas, they suffer condensation to the extent of* $\frac{1}{3}$; *that is, the bulk of the compound formed is only* $\frac{2}{3}$ *that of the original gases from which it was produced, nevertheless the weight of the two volumes so formed, is the total weight of the three volumes that formed them.* Thus—

$$\boxed{H\,H} + \boxed{O} = \boxed{H_2\,O} \text{ or } 2 + 16 = 18.$$
2 vols. + 1 vol. = 2 vols.

This, again, constitutes a type of another group of compounds, such as H_2S, H_2Se, etc.

(3.) $\left.\begin{matrix} H \\ H \\ H \end{matrix}\right\}$ N represents *a molecule of ammonia gas* (*Ammonia Type*).

Whenever 3 *volumes of one gas combine with* 1 *volume of another gas, they suffer condensation to the extent of* $\frac{1}{2}$; *that is, the bulk of the compound formed is only one-half that of the original gases from which it was produced, nevertheless the weight of the two volumes so formed, is the total weight of the four volumes that formed them.* Thus—

$$\boxed{H\,H\,H} + \boxed{N} = \boxed{N\,H_3} \text{ or } 3 + 14 = 17.$$
3 vols. + 1 vol. = 2 vols.

(4.) $\left.\begin{matrix} H \\ H \\ H \\ H \end{matrix}\right\}$ C represents *a molecule of marsh gas* (*Marsh Gas Type*).

Whenever 4 *volumes of one gas combine with* 1 *volume of another gas, they*

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suffer condensation to the extent of $\frac{3}{5}$; *that is, the five volumes, after combination, only measure* 2 *volumes, nevertheless the weight of the two volumes so formed, is the total weight of the five volumes that formed them.* Thus—

$$\underset{4\text{ vols.}}{\boxed{H|H|H|H}} + \underset{1\text{ vol.}}{\boxed{C}} = \underset{2\text{ vols.}}{\boxed{C\,H_4}} \quad \text{or } 4 + 12 = 16.$$

It would thus appear that the molecules of compound bodies in the gaseous state, occupy twice the volume of an atom of hydrogen gas; all compounds, no matter what the number of atoms or volumes may be of which they are composed, becoming condensed into 2 volumes.

Relative Weights of Compound and Elementary Gases.

By the *Specific Gravity* of a gas we imply its weight compared with *air*.

By the *relative weight* of a gas we imply its weight compared with *hydrogen*.

(α.) In the case of the *elementary gases*, it is manifest that their *atomic* weights must be also their *relative* weights. A given volume of oxygen weighs 16 times as much as a similar volume of hydrogen;—16, therefore is the relative weight of oxygen.

(β.) In the case of *compound gases* it must be remembered that after the combination of their constituent elements, *two* volumes are formed. Hence the relative weight of any compound gas is the sum of the weights of the component elements divided by 2. For example, a volume of hydrogen (1) and a volume of chlorine (35·5) form *two* volumes of hydrochloric acid gas. Hence $\left(\frac{36{\cdot}5}{2}\text{ or}\right)$ 18·25 in the relative weight of hydrochloric acid gas;—in other words hydrochloric acid gas is 18·25 times heavier than hydrogen. Similarly water gas is $\left(\frac{18}{2}=\right)$ 9 times heavier than hydrogen, and ammonia gas $\left(\frac{17}{2}=\right)$ 8·5 times, and marsh gas $\left(\frac{16}{2}=\right)$ 8 times heavier. These numbers therefore constitute the relative weights of these compound gases.

Unit of Volume.—The Crith.—Hydrogen, being the lightest known gas, is regarded not only as *the unit of weight*, but as *the unit of volume*. A litre of hydrogen weighs 0·0896 grm., this number being called a crith (κριθή, a barleycorn).

(α.) The weight of a litre of any *elementary* gas, is found by multiplying 0·0896 grm. (*i. e.*, the weight of a litre of hydrogen) by its atomic weight. Thus—

1 Litre of oxygen weighs $0{\cdot}0896 \times 16 = 1{\cdot}433$ grm.
1 Litre of nitrogen ,, $0{\cdot}0896 \times 14 = 1{\cdot}254$ grm.

(β.) The weight of a litre of any *compound* gas is found by multiply-

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ing 0·0896 grm. by *half its molecular weight*, inasmuch as the molecular weight represents two volumes. Thus—

1 Litre of water gas (mol. wt. 18) weighs 0·0896 × 9 = 0·806 grm.
1 Litre of carbonic anhyd. (mol. wt. 44) ,, 0·0896 × 22 = 1·971 grm.
1 Litre of marsh gas (mol. wt. 16) ,, 0·0896 × 8 = 0·716 grm.

II. A gramme (15·432 grains) of hydrogen at 0° C. and at 760 mm. pressure measures 11·2 litres. Therefore the atomic weights of the elementary gases, and half the molecular weights of the compound gases represent in grammes the quantity necessary to occupy 11·2 litres.

(*a.*) 1 grm. of hydrogen measures 11·2 litres,
16 grms. of oxygen measures 11·2 ,,
14 grms. of nitrogen measures 11·2 ,,

(*β.*) $9\left(\frac{18}{2}\right)$ grms. of water gas measures 11·2 litres.

$22\left(\frac{44}{2}\right)$,, of carbonic anhydride measures 11·2 litres.

$8\left(\frac{16}{2}\right)$,, of marsh gas measures 11·2 ,,

Relation between Atomic Weights and Specific Gravity.—So far as *solids and liquids* are concerned, no relationship has as yet been traced between atomic weights and specific gravities, but in the case of *both simple and compound gases* the relationship is definite, and obedient to fixed rules.

(*a.*) *In the case of elementary gases and vapors* we have said that *the atomic weights* of the elements represent *equal volumes* of the elements at the same temperature and pressure. Thus, if $\boxed{H} = 1$; then $\boxed{O} = 16$ and $\boxed{N} = 14$. Or, to state the same truth in another way, 1 grain of hydrogen, 16 grains of oxygen, and 14 grains of nitrogen occupy, the temperature and pressure being uniform, 44·473 cubic inches. If, then, we regard the specific gravity of hydrogen as 1, and employ it as the standard of comparison, it is manifest that *the atomic weights* of the elementary gases and vapors are also *their relative weights*, hydrogen being regarded as the standard of comparison.

But, in stating specific gravities, air, and not hydrogen, constitutes our standard of comparison, and is regarded as equal to 1. Air having a specific gravity of 1, hydrogen is found to have a specific gravity of 0·0694; that is, the specific gravity of air as compared to hydrogen, is as 1 to 0·0694. Therefore, to find the specific gravity of any elementary gas or vapor, all that is necessary is to multiply its atomic weight by 0·0694, the specific gravity of hydrogen.

To find the specific gravity of oxygen, chlorine, and nitrogen:

0·0694 × 16 (atomic weight of oxygen) = 1·1104, Sp. Gr. of oxygen.
0·0694 × 35·5 (,, of chlorine) = 2·4637, ,, of chlorine.
0·0694 × 14 (,, of nitrogen) = 0·9716, ,, of nitrogen.

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There are the following *exceptions* to be noted to this rule—

(1.) The vapor densities of *phosphorus and arsenic* compared to hydrogen are twice their atomic weights; therefore in estimating the specific gravities of these bodies the atomic weights must be doubled—

31=atomic weight of phosphorus; $0{\cdot}0694 \times (31 \times 2) = 4{\cdot}3028$, Sp. Gr. of phos. vapor.
75= „ of arsenic; $0{\cdot}0694 \times (75 \times 2) = 10{\cdot}410$ „ of arsenic „

(2.) The vapor densities of *mercury, zinc, and cadmium* compared to hydrogen, are one-half their atomic weights; therefore, in estimating the specific gravity of these bodies the atomic weights must be halved—

200 = atomic weight of mercury; $0{\cdot}0694 \times \left(\frac{200}{2}\right) = 6{\cdot}94$ Sp. Gr. of mercury vapor.

112= „ of cadmium; $0{\cdot}0694 \times \left(\frac{112}{2}\right) = 3{\cdot}8864$ „ of cadmium „

(β.) *In the case of compound gases and vapors.*—The molecule of a compound body, it must be remembered, is always twice that of the hydrogen atom. Therefore—

$$\frac{\text{Molecular weight} \times 0{\cdot}0694}{2} \text{ or Relative weight} \times 0{\cdot}0694 = \text{Sp. Gr.}$$

Examples:

HCl; $\frac{0{\cdot}0694 \times 36{\cdot}5\ (HCl)}{2} = 1{\cdot}2665$ Sp. Gr. of hydrochloric acid gas.

H_2O; $\frac{0{\cdot}0694 \times 18\ (OH_2)}{2} = 0{\cdot}6246$ Sp. Gr. of water gas.

H_3N; $\frac{0{\cdot}0694 \times 17\ (NH_3)}{2} = 0{\cdot}5899$ Sp. Gr. of ammonia gas.

CO_2; $\frac{0{\cdot}0694 \times 44\ (CO_2)}{2} = 1{\cdot}5268$ Sp. Gr. of carbonic acid gas.

There are certain exceptions to this rule in such compounds as PCl_5 (?)—$SbCl_5$—Hg_2Cl_2, where the molecule occupies 4 volumes and not 2, although this compound of 4 volumes resolves itself by heat into two compounds of 2 volumes each.

Relation between Atomic Weights and Specific Heats.—The "*specific heat*" of a body is the "*quantity of heat*" that a body gives out or takes in, whilst passing from one temperature to another. This is ordinarily determined by taking equal weights of bodies and estimating the quantity of heat required to raise them to a given temperature.

(1.) For purposes of comparison the following standard is adopted *in England*, viz.:—

"*The quantity of heat required to raise* 1 *lb. of water* 1° C."

This 1 pound of water is called "*the unit of weight*," and the 1° C. is called "*the unit of heat*" or "*thermal unit.*" It is clear, therefore, that to raise 1 lb. of water from 0° C. to 100° C. would require 100 units of heat.

(2.) The standard of comparison *in France* is—

"*The quantity of heat required to raise* 1 *kilogramme of water* 1° C."

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A kilogramme being equal to 2·2 lbs., it follows that every *French* unit of heat is equal to 2·2 *English* units of heat.

Water is chosen for purposes of comparison, because (excepting hydrogen) it requires more heat to raise its temperature than any other known substance.

Hence, the quantity of heat necessary to raise 1 lb. of water 1° C. is called 1, and this constitutes our starting-point.

When we say, therefore, that the specific heat of iron is equal to 0·1138 and that of hydrogen to 3·4090, we imply that if it would take—

1·000 unit of heat to raise 1 lb. of water 1° C.; it would require

0·1138 ,, ,, 1 lb. of iron 1° C.; or

3·4090 ,, ,, 1 lb. of hydrogen 1° C.

Now it is found that although the numbers obtained as the specific heats of different bodies are very dissimilar, there is a remarkable uniformity in the products of the specific heats when multiplied by the several atomic weights. This number is termed the *atomic heat* of the body, and in the case of the elementary bodies commonly varies not more than from 6 to 7.

SPECIFIC HEATS OF ELEMENTARY BODIES.

Elements.	Specific Heat. (that of Water=1).	Atomic Weights.	Product of Sp. Heat × At. Weight.
Lithium	0·9408	7·	6·59
Sodium	0·2934	23·	6·75
Aluminium	0·2143	27·4	5·89
Phosphorus { liquid	0·2120	31·	6·57
Phosphorus { solid	0·1887	31·	5·85
Sulphur	0·2026	32·	6·48
Potassium	0·1696	39·	6·61
Iron	0·1138	56·	6·37
Nickel	0·1086	58·8	6·37
Cobalt	0·1070	58·8	6·28
Copper	0·0952	63·4	6·04
Zinc	0·0956	65·2	6·24
Arsenic	0·0814	75·	6·10
Selenium	0·0762	79·4	6·02
Bromine (solid)	0·0843	80·	6·75
Palladium	0·0593	106·6	6·31
Silver	0·0570	108·	6·16
Cadmium	0·0567	112·	6·35
Indium	0·0570	113·4	6·46
Tin	0·0562	118·	6·63
Antimony	0·0508	122·	6·19
Iodine	0·0541	127·	6·87
Tellurium	0·0474	128·	6·06
Gold	0·0324	197·	6·38
Platinum	0·0311	197·4	6·15
Mercury { solid	0·0319	200·	6·38
Mercury { liquid	0·0333	200·	6·66
Thallium	0·0335	204·	6·83
Lead	0·0314	207·	6·50
Bismuth	0·0308	210·	6·48

It will thus be seen that the specific heats of these several bodies multiplied by their atomic weights, produce an almost constant

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product. We may conclude from this that probably all atoms require the same amount of heat to raise their temperature one degree. This result accords with the surmises of Dulong and Petit, who thought that the atoms of all elementary bodies had the same atomic weight.

Thus far the law may be stated as follows: "*The specific heats of elementary bodies is inversely as their atomic weights.*"

There are, however, some apparent *exceptions*, as will be seen in the following table, although the results obtained by Professor Weber point to the fact that these bodies at high temperatures obey the law of Dulong and Petit. ("Quarterly Journal of Science," Jan., 1876.)

	Specific Heat (Water=1).	Atomic Weight.	Product of Sp. Heat × At. Weight.
Boron	0·2500	× 11 =	2·75
Hydrogen	3·29	× 1 =	3·29
Nitrogen	0·27	× 14 =	3·78
Oxygen	0·23	× 16 =	3·68
Carbon (charcoal .. ..)	0·2415	× 12 =	2·96
Carbon (graphite .. ..)	0·2008	× 12 =	2·41
Carbon (diamond .. ..)	0·1469	× 12 =	1·76
Silicon	0·1774	× 28 =	4·97

In the case of *compounds* of similar atomic composition and constitution, the specific heats are also inversely as their atomic weights.

Atomicity or Quantivalence.—The terms *quantivalence* (*quanti* and *valeo*), *dynamicity*, or *atomicity* imply, that although the symbol of an element (such as O, N, etc.), represents an atom of that element, the atom having an unchangeable *relative* weight (for of the *absolute* weights of the atoms we know nothing with certainty), nevertheless, that such symbol does not express "the *valence*" or "*chemical value*," or "*power*" of such atom, this power varying with different bodies.

Thus in *hydrochloric acid* (HCl), 1 of chlorine is satisfied with, or, in other words, has the same value as, 1 of hydrogen. Under no circumstances can 1 of chlorine combine with more than 1 of hydrogen. But in water (H_2O) we find that 1 of oxygen is not satisfied with less than 2 of hydrogen, whilst in marsh gas (CH_4) the carbon atom is not satisfied with less than 4 of hydrogen. Thus it is evident that the power of carbon, as represented by the symbol C, is chemically equal to 4 hydrogens, or (H_4), the symbol O being chemically equal to 2 hydrogens (H_2), and the symbol Cl to 1 hydrogen (H). The terms *quantivalence*, *dynamicity*, or *atomicity* express, therefore, the fact that an atom of one element may be chemically equal to, and have the power of fixing, one or more atoms of other elements.

Further, we must note that the term *equivalent* (*æquus*, equal, and *valeo*, I am worth) is not synonymous with *atomic weight*, for whilst hydrogen, oxygen, and carbon have atomic weights of 1, 16, and 12 respectively, nevertheless, 1 of carbon is equivalent to 2 of oxygen and to 4 of hydrogen, whilst 1 of oxygen is equivalent to 2 of hydrogen.

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The value or atomicity of bodies is often indicated by what are called *graphic formulæ*, the valence of an element being represented by lines or bonds, expressive of what Frankland calls its atom-fixing power.

Thus, Cl—, —O—, —C(|)—, represent graphically chlorine as a monad with one bond, oxygen as a dyad with two bonds, and carbon as a tetrad with four bonds. Chlorine, we know, can only fix one atom of hydrogen to form a molecule of HCl (thus Cl—H=HCl), whilst oxygen can fix two hydrogen atoms to form a water molecule ($H—O—H=OH_2$), and carbon can fix four hydrogen atoms to form a marsh gas molecule, $\begin{matrix} & H & \\ & | & \\ H—C—H \\ & | & \\ & H & \end{matrix}=(CH_4)$. Thus the lines are expressive of the atomicity of a body, and are to be regarded as pictures representing the number of bonds, and how they are severally utilized.

No element can exist with its bonds unconnected or dissatisfied. It is clear, therefore, that the molecule of every element possessing an uneven number of bonds (*i. e.*, being a perissad) must consist of two or more atoms united. You cannot have hydrogen in a free state thus —H; but you can have it thus, H—H. Hence we regard H_2 as the hydrogen molecule, and not H. In the case of an *artiad, i.e.*, an element possessing an even number of bonds, the molecule may consist of one atom (*monatomic*), inasmuch as the bonds, by combining amongst themselves, may satisfy each other, and so become latent. Thus, a molecule of oxygen may be represented as —O—; whilst, on the other hand, it must be remembered that the oxygen molecule may also be *diatomic*, represented thus, O=O, or *triatomic* (as in the case of ozone), represented thus $\begin{matrix} & O & \\ & \diagup\diagdown & \\ O—O \end{matrix}$ (*polyatomic*).

Glyptic formulæ are merely material illustrations of graphic formulæ, where atoms are represented by balls, and lines by wires.

METHOD OF DETERMINING THE QUANTIVALENCE OR ATOMICITY OF A BODY.

Agreeing to understand by the quantivalence of a body, the number of univalent atoms with which the symbol representing its atomic weight can unite, we determine this quantivalence in such ways as the following:—

(1.) *By the number of hydrogen atoms with which a body can combine to form a molecule.*

Example. 1 of hydrogen combines with 1 of chlorine. Therefore the valence of chlorine = the valence of hydrogen.

(2.) *If an element will not combine with hydrogen, but will combine with chlorine, its valence may then be determined by the number of chlorine atoms with which it will combine to form a molecule.*

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Example. 1 atom of silver (Ag) combines with 1 atom of chlorine, and in that proportion only. But silver will not combine with hydrogen; inasmuch, however, as 1 of chlorine combines with 1 of hydrogen, and 1 of chlorine also combines with 1 of silver, if ever silver could be made to combine with hydrogen, we infer it would do so in the proportion of 1 atom of hydrogen to 1 atom of silver. We may express these facts thus—

(1.) The valence of silver=the valence of chlorine;
(2.) The valence of chlorine=the valence of hydrogen;
Therefore (3.) The valence of silver=the valence of hydrogen.

It will thus be seen that hydrogen, chlorine, and silver are equivalent.

(3.) *By the proportion of hydrogen which a body can replace in a saline molecule.*

Examples. (*a.*) A water molecule is made up of 2 atoms of hydrogen and 1 of oxygen. One or both of the hydrogen atoms may be replaced by an alkaline metal, such as potassium. Thus—

$$\left.\begin{matrix}H\\H\end{matrix}\right\} O = H_2O; \quad \left.\begin{matrix}H\\K\end{matrix}\right\} O = KHO; \quad \left.\begin{matrix}K\\K\end{matrix}\right\} O = K_2O$$

It is clear, therefore, that the value or valence of potassium is identical with the value of hydrogen.

(*b.*) Again: calcium, zinc, or barium may also be made to take the place of hydrogen, but under such circumstances it will be found that 1 atom of these elements is equivalent to 2 atoms of hydrogen. Thus—

$$\left.\begin{matrix}H\\H\end{matrix}\right\} O = H_2O; \quad Ca''O \text{ (not } Ca_2O); \quad Zn''O \text{ (not } Zn_2O).$$

Hence, the valence of calcium or of zinc is double that of hydrogen, inasmuch as 1 of zinc or 1 of calcium can replace 2 of hydrogen in a molecule.

Looking, therefore, at these facts, it is clear that the elements have very different values in their capacities for substitution displacement. Agreeing to regard hydrogen as our standard of equivalence, it is evident that the elements are susceptible of arrangement into groups.

Group I.

Certain elements are *univalent;* that is, 1 atom in chemical exchange is equal in value to 1 atom of *hydrogen* or other univalent element. Such bodies are called *monad elements.*

Group II.

Certain elements are *divalent;* that is, 1 atom in chemical exchange is equal to, and may replace, either (*a*) 2 atoms of hydrogen, or 2 atoms of any other monad; or (*b*) 1 atom of any other divalent element. Such bodies are called *dyad elements.*

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Group III.

Certain elements are *trivalent;* that is, 1 atom in chemical exchange is equal to (*a*) 3 atoms of hydrogen or other monad element; or to (*b*) 1 atom of a divalent element + 1 atom of a monad element. Such bodies are called *triad elements*.

Group IV.

Certain elements are *quadrivalent;* that is, 1 atom in chemical exchange is equal to (*a*) 4 atoms of hydrogen or other monad element; or to (*b*) 2 atoms of oxygen or other dyad element; or to (*c*) 1 atom of a dyad+2 atoms of a monad element; or to (*d*) 1 atom of a triad +1 atom of a monad element.

Groups V. and VI.

Certain elements are *quinquivalent* and *hexivalent;* that is, 1 atom in chemical exchange is equal to 5 and to 6 atoms of hydrogen or their respective equivalents.

We have borrowed from Dr. Frankland's Lecture Notes the following diagram, representing at a glance the atomicity of the elements. The metalloids are printed in thick type, and the metals in ordinary Roman type.

TABLE OF ATOMICITIES (Frankland,)

Monads.	Dyads.	Triads.	Tetrads.	Pentads.	Hexads.
I. **Hydrogen.**	I. **Oxygen.**	I. **Boron.**	I. **Carbon.** **Silicon.** Tin. Titanium.	I. **Nitrogen.** **Phosphorus.** Vanadium. Arsenic. Antimony. Bismuth.	I. **Sulphur.** **Selenium.** Tellurium.
II. **Fluorine.** **Chlorine.** **Bromine.** **Iodine.**	II. Barium. Strontium. Calcium. Magnesium. Zinc.	II. Gold. III. Thallium.	II. Thorium. Niobium. Tantalum. Zirconium. Aluminium. Indium.		II. Tungsten. Molybdenum.
III. Cæsium. Rubidium. Potassium. Sodium. Lithium.	III. Didymium. Lanthanum. Yttrium. Glucinum.		III. Platinum. Palladium.		III. Osmium. Iridium. Ruthenium. Rhodium.
IV. Silver.	IV. Cadmium. Mercury. Copper.		IV. Lead.		IV. Chromium. Manganese. Iron. Cobalt. Nickel. Uranium. Cerium.

Although we thus arrange elements in their several classes according to their value as best we know them, it must not be supposed that we are in a position to fix their several positions definitely. In some cases *the valence of an element varies: Carbon,* for example, in marsh

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gas is a tetrad ($C^{iv}H_4$). So also it is a tetravalent in carbonic anhydride ($C^{iv}O_2$), whilst in carbonic oxide ($C''O$) it plays the part of a dyad. *Nitrogen*, again, may act as a monad, as in N_2O, or as a triad, as in NH_3, or as a pentad, as in NH_4Cl. Admitting that these variations are difficult of explanation and somewhat interfere with general conclusions, we may note, as Dr. Frankland remarks, that the variation always takes place by the disappearance or development of an even number of bonds. Thus nitrogen may be a monad (—N), a triad (—N—), or a pentad (N); it is never a dyad, or a tetrad. Carbon may be a dyad (—C—), or a tetrad (—C—), but it is never a monad or a triad. In short, a perissad is never an artiad, or an artiad a perissad. Dr. Frankland explains these variations by supposing that some of the bonds may unite and become latent. Thus nitrogen with its five bonds (N) becomes a triad by the union of two; thus (N). In this way Dr. Frankland distinguishes between *latent atomicity*, or the number of conjoined bonds; *active atomicity*, or the total number of bonds in actual combination with other elements; and *absolute atomicity*, the sum of the latent and the active atomicities. Whenever an element is fully saturated, that is, has received its full value of other elements, the body so formed is more stable than when its valence is not fully satisfied. Thus CO_2 is a more stable body than CO. Hence the true valence of an element is always indicated by the largest number of hydrogen or other monad elements with which it can combine. The valence, moreover, must not be determined from oxides or from sulphides, because each dyad, made up as it is of two units of equivalency, neutralizes one unit in the compound it enters, and introduces a second unit, leaving the equivalence as it was before.

For convenience these several groups are divided under the two heads of *Odds* and *Evens*.

(1.) *Odds* or *Perissads* (περισσὸς, odd) { Monads. Triads. Pentads.

(2.) *Evens* or *Artiads* (ἄρτιος, even) { Dyads. Tetrads. Hexads.

The quantivalence of bodies is usually denoted by placing dashes or Roman figures to the right of the symbol. Thus H′ with one dash means that hydrogen is a monad; O″ with two dashes that oxygen is a dyad; whilst C^{iv} shows carbon to be a tetrad, and so forth.

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Chemical Formulæ.

The object of chemical formulæ is to express the composition and the probable constitution of a chemical substance. Formulæ are of two kinds—

(1.) *Experimental or empirical.*
(2.) *Theoretical or rational.*

I. Experimental or Empirical Formulæ.

An empirical formula represents merely by the smallest integers the number of atomic proportions of the several elements present in a body. It is the expression of the actual experimental results of analysis. An empirical formula in no way represents the groupings of the elements. We give an illustration in detail of the determination of the empirical formula of magnesic sulphate.

(1.) *Determine percentage composition.* On analysis, we should find in every 100 parts of magnesic sulphate—

Magnesic oxide (magnesia) . .	16·26
Sulphuric anhydride	32·52
Water	51·22=100·00

(2.) *Divide these numbers* (*i.e.*, the percentage numbers) *severally by their atomic weights.* Thus, 40, 80, and 18 represent respectively the atomic weights of magnesia, sulphuric anhydride, and water; therefore—

$$\frac{16\cdot26}{40}=\cdot4065; \qquad \frac{32\cdot52}{80}=\cdot4065; \qquad \frac{51\cdot22}{18}=2\cdot845.$$

(3.) *Reduce the quotients thus obtained to their simplest expression.* Thus—

	Magnesia.	Sulphuric anhydride.	Water.
The ratio of the numbers	0·4065	0·4065	2·845
corresponds to	1	1	7

From which it is clear that the relative atomic proportion of magnesia (MgO) to sulphuric anhydride (SO_3) is as 1 to 1, and of these to water (H_2O) as 1 to 7. Thus, $MgO+SO_3+H_{14}O_7$ or $MgSO_{11}H_{14}$ represents the experimental or empirical formula for magnesic sulphate. Hence the rules to determine the empirical formula of a body may be thus summarized—

(1.) Determine by analysis its percentage composition.
(2.) Divide the numbers so obtained by their atomic weights.
(3.) Reduce the quotients to their simplest expression.

II. Rational or Theoretical Formulæ.

Such formulæ represent not only the elements present and their atomic proportions, but the manner (according to every man's views or fancies) in which these elements are grouped. Thus, magnesic sulphate may be written MgO, SO_3, $7H_2O$, or $MgSO_4,H_2O,6H_2O$, and

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in many other ways; and it may be judged if different opinions exist as to the exact method of expressing the theoretical formula of so simple a body as magnesic sulphate, what a play there is for imagination in the expression of the formulæ of complex organic bodies. For example, there are nineteen different ways of representing acetic acid ($C_2H_4O_2$). Such formulas are as yet merely *theoretical formulas*, and although in many cases true, and in many other cases the approach to truth, must be received with caution.

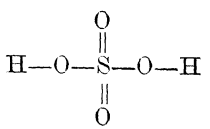
Of late what are called *constitutional formulæ*, as suggested by Dr. Frankland, have found favor with chemists, and, inasmuch as we have in part adopted their use, it is necessary to explain them in detail.

A *constitutional formula* is designed to give us some idea of the arrangement of atoms in a molecule. In a constitutional formula the symbol of the principal element is placed first, thereby denoting that the several elements, or compound radicals following it on the same line, are held to it, as the principal element of the molecule, by what Frankland terms bonds. We may thus regard the molecule as a family, and the principal element, as the parent or head of the family. Further, to distinguish constitutional formulæ from molecular or empirical formulæ, the head of the family, or the principal bondholder or bondholders are printed in thick type. A few illustrations will render this clear:—

OH_2 is the constitutional formula for water, and implies that the dyad atom oxygen is the parent bondholder, or grouping element, of the water molecule, and is combined by bonds to each hydrogen atom. Graphically it may be symbolized thus, H—O—H.

SO_2Ho_2 is the constitutional formula for sulphuric acid. Here sulphur is the parent bondholder, having six bonds (hexad), four of which are united with the four bonds from the two oxygen atoms (oxygen being a dyad), and two with the bonds of the two half molecules of hydroxyl (Ho).

Graphically it may be symbolized thus,



It will thus be seen that constitutional formulæ are merely methods of representing glyptic and graphic formulæ symbolically.

In expressing many constitutional formulæ a bracket is used. Thus, potassic chlorate ($KClO_3$) is represented either—

(*a.*) as $\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ko,\end{matrix}\right.$ which means that one bond from each oxygen atom (oxygen being a dyad) is joined to 1 of chlorine and to 1 of potassoxyl (Ko) respectively, whilst the two atoms of oxygen are united together by 1 bond from each.

Graphically the constitutional formula $\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ko\end{matrix}\right\}$ may be expressed thus $\left\{\begin{matrix}O—Cl\\ |\\ O—Ko\end{matrix}\right.$; or

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(β.) as $\left\{\begin{matrix}\mathrm{OCl}\\ \mathrm{O}\\ \mathrm{OK}\end{matrix}\right.$ or graphically as $\begin{matrix}\mathrm{O{-}Cl}\\ |\\ \mathrm{O}\\ |\\ \mathrm{O{-}K}\end{matrix}$ which implies—

that one of the bonds of the first oxygen atom is combined with the monad chlorine, and the other with one bond from a second oxygen atom, the other bond of which is combined with a third oxygen atom, this last having its second bond united with the potassium atom. Thereby all bonds are satisfied.

Substitution (*Substitutus*, put in another's place).

(A.)—**Inorganic.**—Having regard to the molecular constitution of matter, we find that, in mineral chemistry, the several constituents of a molecule may be replaced (*i.e.* substituted) by their equivalent of other bodies, without changing the typical constitution of the original molecule. Thus—

(1.) $\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}$ represents a molecule of *hydrogen*.

(α.) One hydrogen atom (monad) of this *hydrogen* molecule may be replaced by a haloid atom (monad) to form the hydracids; thus—

$$\mathrm{HH}\ ;\quad \mathrm{HCl}\ ;\quad \mathrm{HBr}\ ;\quad \mathrm{HI}\ ;\quad \mathrm{HF}.$$

(β.) One hydrogen atom may also be replaced by an alkaline metal, to form a hydride.

(2.) $\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}$ ($=\mathrm{H_2O}$) represents a molecule of *water*.

(α.) One or both hydrogen atoms of this *water* molecule may be replaced by an alkaline metal; thus—

$$\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\ ;\quad \overbrace{\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\ ;\quad \left.\begin{matrix}\mathrm{Na}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}}^{\text{Hydrates}}\ ;\quad \overbrace{\left.\begin{matrix}\mathrm{K}\\ \mathrm{K}\end{matrix}\right\}\mathrm{O}\ ;\quad \left.\begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix}\right\}\mathrm{O}}^{\text{Oxides}}.$$

(β.) Two hydrogen atoms may be replaced by one of a dyad element; thus—

$$\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\ ;\quad \mathrm{Zn''O}\ ;\quad \mathrm{Ca''O}\ ;\quad \mathrm{Ba''O}.$$

(γ.) The dyad oxygen may be replaced by the dyads sulphur, selenium, or tellurium; thus—

$$\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\ ;\quad \left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\ ;\quad \left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{Se}\ ;\quad \left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{Te}.$$

(3.) $\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{N}$ ($=\mathrm{NH_3}$) represents a molecule of *ammonia*.

(α.) The three hydrogen atoms of this *ammonia* molecule may be replaced by three chlorine, bromine, or iodine atoms; thus—

$$\mathrm{NH_3}\ ;\quad \mathrm{NCl_3};\quad \mathrm{NBr_3}\ ;\quad \mathrm{NI_3}.$$

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(β.) A part only of the hydrogen may be replaced by a metal, or by a compound radical; thus—

NH_3; NH_2K (Potassamide); $(SO_2(NH_2)_2)$ (Sulphamide).

(γ.) The nitrogen may be wholly or partially replaced by phosphorus, arsenic, antimony, and perhaps by bismuth.

(4.) $\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}C$ ($=CH_4$) represents a molecule of *marsh gas.*

Here substitutions are endless, as we shall note more particularly under organic chemistry.

(5.) In the formation of salts, the hydrogen of an acid is replaced by one or more atoms of a metal or compound positive radical; thus—

(α.) *Sulphuric acid* contains two displaceable atoms of hydrogen (H_2SO_4).

1 hydrogen may be displaced by 1 of potassium (monad) forming $HKSO_4$ (*acid salt.*)
2 hydrogens „ „ 2 of „ („) „ K_2SO_4 (*normal salt.*)
2 hydrogens „ „ 1 of calcium (dyad) „ $CaSO_4$

(β.) *Phosphoric acid* contains three displaceable atoms of hydrogen (H_3PO_4).

3 hydrogens may be displaced by 3 of silver (monad) Ag_3PO_4
2 „ „ 2 of sodium („) HNa_2PO_4
1 „ „ 1 of „ („) NaH_2PO_4

Similarly, 1 triad will take the place of 3 monads, or 1 dyad of 2 monads.

(B.) **Organic.**—The substitution of compound radicals for elements, forms a remarkable feature in organic chemistry. Liebig defined organic chemistry as "*the chemistry of compound radicals.*"

(1.) One of the hydrogen atoms of a hydrogen molecule (HH) may be replaced by such compound radicals as Methyl (CH_3), Ethyl (C_2H_5), Propyl (C_3H_7), etc., whereby a hydride of the organic radical is formed. Thus—

$(CH_3)H$ = *Methyl-hydride*; $(C_2H_5)H$ = *Ethyl-hydride*; $(C_3H_7)H$ = *Propyl-hydride.*

Further, the hydrogen of these compounds may be replaced by chlorine or cyanogen. Thus—

$(CH_3)Cl$ = *Methyl-chloride*; $(C_2H_5)Cl$ = *Ethyl-chloride*; $(C_3H_7)Cl$ = *Propyl-chloride.*
$(CH_3)Cy$ = *Methyl-cyanide*; $(C_2H_5)Cy$ = *Ethyl-cyanide*; $(C_3H_7)Cy$ = *Propyl-cyanide.*

(2.) In the alcohols and ethers, we find bodies constructed on the water (H_2O) type.

(α.) One hydrogen of a water molecule may be replaced by a compound radical to form an *alcohol*; thus—

$\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O$ = *Methyl alcohol*; $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$ = *Ethyl alcohol.*

(β.) Both atoms of hydrogen may be replaced by two of the compound radical to form an *ether*; thus—

$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O$ = *Methyl ether*; $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$ = *Ethyl ether.*

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(γ.) Or the oxygen may be replaced by sulphur, and perhaps by selenium; thus—

$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S$ = Ethylic sulphydrate (Mercaptan.); $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}S$ = Ethylic sulphide (Sulphur ether.)

(δ.) Or the oxygen may be replaced by silicon, or by a metal, whereby the metallic ethyls, etc., are produced; thus—

$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}Zn$ = Zincic methide. $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Hg$ = Mercuric ethide.

(3.) Bodies constructed on the ammonia (NH_3) type are found in the amides and in the alcoholic ammonias.

(α.) One or more atoms of hydrogen may be replaced by one or more compound radicals, such as ethyl (C_2H_5); thus—

$\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N$ = Ethylamine; $\left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}N$ = Diethylamine;

$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}N$ = Triethylamine.

(β.) One or more atoms of hydrogen may be replaced by an oxydized radical, as in the "amides," or else by different radicals; thus—

$\left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N$ = Acetamide (called a primary amide.); $\left.\begin{matrix}C_2H_3O\\C_2H_3O\\H\end{matrix}\right\}N$ = Diacetamide (called a secondary amide.);

$\left.\begin{matrix}C_2H_3O\\C_2H_3O\\C_2H_5\end{matrix}\right\}N$ = Ethylic Diacetamide.

(γ.) The nitrogen may be replaced by arsenic, antimony, bismuth, etc., as follows:—

$\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}As$ = Trimethylarsine; $\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}Sb$ = Triethyl-stibine;

$\left.\begin{matrix}CH_3\\H\\H\end{matrix}\right\}P$ = Methyl-phosphine.

(4.) In the case of the marsh gas (CH_4) molecule, the substitutions are without number, the hydrogens being replaced in almost endless variety.

Isomerism (ἴσος equal, μέρος a part).

Isomerism is a term applied to bodies containing the same elements, united in the same proportions, but differing more or less widely in their physical, physiological, and chemical properties.

Isomerides are of two classes:—

(1.) Where the *percentage* composition is similar, but the *molecular* composition dissimilar (polymers);

(2.) Where both the percentage and the molecular compositions are alike (metamers).

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I. *Isomerides having similar percentage but different molecular composition; in other words, having different vapour densities* (Polymerism). Examples of such isomerides (polymers) are seen in the following cases:—

(α.) *Cyanogen* (CN or $C\bar{y}$), a poisonous gas, and *Paracyanogen* (C^nN^n or $C\bar{y}^n$), an inert solid, alike contain in every 100 parts—

Carbon 46·15; Nitrogen 53·85.

(β.) *The chlorides of Cyanogen, viz:*—

$CyCl$ = gaseous chloride of cyanogen,
Cy_2Cl_2 = liquid ,, ,,
Cy_3Cl_3 = solid ,, ,,

have a similar percentage composition, viz.:—

Carbon, 19·51; Nitrogen, 22·77; Chlorine, 57·72.

Further illustrations of polymerism may be found in the cyanogen oxyacids (viz., cyanic, fulminuric, and cyanuric acids, and cyamelide); also in the various hydrocarbon series, and in numerous other cases.

II. *Isomerides having an identical percentage and molecular composition* (Metamerism). These bodies, consequently, have similar vapour densities. Examples of such isomerides (metamers) are seen in the following cases:—

(α.) *Urea* [$(2NH_2)CO$] and *ammonic cyanate* [$CN(NH_4O)$], both of which are represented by the formula CH_4N_2O, contain in every 100 parts—

Carbon	...	...	...	20·00
Hydrogen	...	...	...	6·67
Nitrogen	...	...	...	46·66
Oxygen	...	...	...	26·67=100·00

(β.) The "*turpenes*" (which include oils of turpentine, lemons, bergamot, neroli, lavender, pepper, camomile, carraway, cloves, etc.), have all a similar composition ($C_{10}H_{16}$).

(γ.) *Tartaric acid* (which turns the plane of polarized light to the right, and is hence called dextro-tartaric acid); *racemic acid* (which has no action on a ray of polarized light); *paratartaric acid* (which turns the ray to the left, and is hence known as levo-tartaric acid), have a similar percentage and molecular composition ($C_4H_6O_6$).

(δ.) *Morphia* (the active principle of opium) and *piperine* (the active principle of pepper), are both represented by the formula $C_{17}H_{19}NO_3$.

We may note that these isomerides are divisible into two classes:—

1. *Bodies differing in physical properties, but behaving alike under the action of chemical reagents.* Such, for example, are the turpenes, a series of true isomerides; and

2. *Bodies differing in physical properties, and also behaving differently under the action of chemical reagents.* In such bodies we note the presence of different radicals. For example, propionic acid, methyl acetate, and ethyl formate are isomeric ($C_3H_6O_2$), but their behaviour respectively with potassic hydrate is vastly different. Thus—

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1 Propionic acid with potassic hydrate yields potassic propionate.
2 Methyl acetate ,, ,, potassic acetate and methyl alcohol.
3 Ethyl formate ,, ,, potassic formate and ethyl alcohol.

Isomorphism (ἴσος equal, and μορφή a form).

Acids may frequently be substituted for acids, and bases for bases, in a body, without the body undergoing any alteration of form. Thus, in common potash-alum ($K_2Al_24SO_4,24H_2O$), the K_2 may be replaced by Na_2, or by $(NH_4)_2$, and the Al_2 by Fe_2, Mn_2, or Cr_2, etc., without any change of form resulting. Bodies that crystallize in the same form, and which are similar in chemical constitution, are termed *Isomorphous*.

It has been suggested (Blake, B. Assoc., 1846) that there is a relationship between the physiological action of bodies and their isomorphic condition. Thus, arsenic acid can replace phosphoric acid in the human body, the latter acid being a normal constituent. Hence, arsenic acid is not a poison; whilst arsenious acid, having no homologue in the human body, acts as a poison.

Allotropism (ἄλλος another, and τροπή twist or turn).

The capability of *compound* bodies, having the same percentage and molecular composition, of existing in more than one shape, to which we have alluded under the term isomerism, finds its parallel amongst the *elementary* bodies. Some elements assume various and well marked modifications. Berzelius has termed this *allotropism*, which bears the same relationship to the *element* as *isomerism* does to the *compound*. The existence of *carbon* as charcoal, graphite, and the diamond; the varieties of *phosphorus; sulphur* in its various modifications, or *oxygen*, as common oxygen and as ozone, are illustrations of allotropism.

The Metric System (Unit of Length).

The mètre (*unit of length*) is a bar of platinum deposited in the archives of Paris measuring 39·37 English inches. It is adopted as a measure of length, surface, weight, and capacity.

I. As a Measure of Length.

Its *multiples* are marked by *Greek* prefixes, and its *subdivisions* by *Latin* prefixes.

	In English Inches.	In English Feet.	In English Yards.	In English Miles.
Millimètre	0·03937	0·003281	0·0010936	0·0000006
Centimètre	0·39370	0·032809	0·0109363	0·0000062
Decimètre	3·93708	0·328099	0·1093633	0·0000621
Mètre	39·37079	3·280890	1·0936331	0·0006214
Décamètre	393·70790	32·808992	10·9363310	0·0062138
Hectomètre	3937·07900	328·089920	109·3633100	0·0621382
Kilomètre	39370·79000	3280·899200	1093·6331000	0·6213824
Myriomètre	393707·90000	32808·992000	10936·3310000	6·2138244

1 inch = 2·539954 centimètres.
1 foot = 3·0479449 decimètres.
1 yard = 0·9143835 mètres.
1 mile = 1·6093149 kilomètres.

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II. As a Measure of Surface.

	In English square feet.	In English square yards.	In English acres = 43560 sq. feet.
1 square mètre (Centiare)	10·764299	1·196033	0·0002471
100 square mètres (Are) ..	1076·429934	119·604326	0·0247114
10,000 square mètres (Hectare)	107642·993418	11960·432602	2·4711431

1 square inch = 6·4513669 square centimètres.
1 square yard = 0·83609715 square mètre.
1 square foot = 9·2899683 square decimètres.
1 acre = 0·40467102 hectare.

III. As a Measure of Capacity.

A cubic decimètre (that is, a cube each side of which measures 3·937 inches) holds *a litre* of water at 4° C. (*i.e.*, the temperature at which water is at its maximum density). This litre weighs 1 kilogramme, or 1,000 grammes. A cubic centimetre, therefore, holds a gramme of water at 4° C.

	In cubic inches.	In cubic feet = 1728 cubic inches.	In pints = 34·65923 cubic inches.	In gallons = 8 pints = 277·27384 cubic inches.	In bushels = 8 gallons = 2218·19078 cubic inches.
Millilitre or a cubic centimètre..	0·06103	0·000035	0·00176	0·0002201	0·0000275
Centilitre or 10 cubic centimètres	0·61027	0·000353	0·01760	0·0022009	0·0002751
Décilitre or 100 cubic centimètres	6·10271	0·003532	0·17607	0·0220096	0·0027512
Litre or cubic decimètre	61·02705	0·035317	1·76077	0·2200966	0·0275120
Décalitre (centistère or 10 litres	610·27052	0·353166	17·60773	2·2009667	0·2751208
Hectolitre (Decistère or 100 litres	6102·70515	3·531658	176·07734	22·0096676	2·7512084
Kilolitre or cubic mètre	61027·05152	35·316581	1760·77341	220·0966767	27·5120845
Myriolitre (Décastère	610270·51519	353·165807	17607·73414	2200 9667675	275·1208459

1 cubic inch = 16·386176 cubic centimètres.
1 cubic foot = 28·315312 cubic decimètres.
1 gallon = 4·543358 litres.

IV. As a Measure of Weight.

A cubic centimètre (that is, a vessel, each side of which measures 0·3937 inches) holds a quantity of water which at 4° C. (the maximum density of water) weighs 1 gramme (15·432 grains).

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Measures of Weights.

	In grains.	In ounces Troy = 480 grains.	In pounds avoirdupois =7000 grs.	In cwts.= 112 lbs.= 784000 grs.	In tons= 20 cwts.= 15680000 grs.
Milligramme ..	0·01543	0·000032	0·0000022	0·0000000	0·000000001
Centigramme ..	0·15432	0·000321	0·0000220	0·0000002	0·00000001
Decigramme ..	1·54323	0·003215	0·0002204	0·0000019	0·0000001
Gramme	15·43234	0·032150	0·0022046	0·0000196	0·000001
Decagramme ..	154·32349	0·321507	0·0220462	0·0001968	0·0000098
Hectogramme ..	1543·23488	3·215072	0·2204621	0·0019684	0·0000984
Kilogramme.. ..	15432·34880	32·150726	2·2046212	0·0196841	0·0009842
Myriogramme ..	154323·48800	321·507267	22·0462126	0·1968412	0·0098421

1 grain = 0·064799 grammes.
1 oz. troy =31·103496 grammes.
1 lb. avoirdupois = 0·453495 kilogrammes.
1 cwt. =50·802377 killogrammes.

A kilogramme (=1000 grammes) is about equal to 2¼ lbs. avoirdupois and 1000 kilogrammes are nearly equal to 1 ton.

The following figure will represent the metre in this threefold capacity as a measure of length, capacity, and weight.

3·937 inches = decimètre.

3·937 inches.

Measure of Length— { A mètre = 10 times the length of one side of this figure.

Each side (3·937 inches) = 1 decimètre.
= 10 centimètres.
= 100 millimètres.

Measure of Capacity—

A cubic vessel, each side having the dimensions of this figure would hold 1 litre.

Measure of Weight—

A cubic centimètre of water weighs 1 gramme = 15·432 grains.
1000 ,, = 1 litre or 15,432 grains.

Square Centimètre.

1 centimètre.

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We shall consider in Section I. *the metalloids*, commencing with oxygen. In each case the compounds that the body forms with those elements already considered, will be examined in detail. Each element and compound will be examined as far as practicable in the following order: (1) Synonyms; (2) History; (3) Natural History; (4) Preparation; (5) Properties; (α) sensible; (β) physical; (γ) chemical; (6) Tests; (7) Uses in Nature, Arts, and Medicine.

In Section II. we shall consider *the metals*, their compounds amongst themselves (alloys and amalgams) and their compounds with the non-metals (salts).

Section III. will be devoted to *Organic Chemistry*.

We shall examine the non-metals in the following order:—

	Symbol.	Atomic Weight.	Relative Weight.		Symbol.	Atomic Weight.	Relative Weight.
Oxygen	O.	16	16	Sulphur	S.	32	32
Fluorine ..	F.	19	19	Selenium ..	Se.	79·5	79·5
Chlorine ..	Cl.	35·5	35·5	Tellurium ..	Te.	129	129
Bromine....	Br.	80	80	Carbon	C.	12	
Iodine	I.	127	127	Boron.....	B.	11	
Nitrogen ..	N.	14	14	Silicon	Si.	28	
Phosphorus	P.	31	62	Hydrogen ..	H.	1	1

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SECTION I.—THE METALLOIDS.

CHAPTER III.

OXYGEN.

OXYGEN:—Synonyms—History—Natural History—Preparation—Properties. OZONE: History—Natural History—Preparation—Properties—Tests—Quantitative Determination—Uses of Oxygen—Respiration—Combustion.

OXYGEN (O″=16).

Atomic weight=16. *Molecular weight*=32. *Dyad″* (H_2O—Ag_2O). *Molecular volume* $\square$. *Relative weight* (H=1) 16. *Specific gravity* (*Air*=1) *observed* 1·1056; *theoretic* (0·0693 × 16) 1·1088. 1 *Litre weighs* 16 *criths* (0·0896 *grm.* × 16)=1·4336 *grm. at* 0°*C. and* 766 *millimetres;* 100 *cubic inches weigh at* 60° *F. and* 30 *B. P.* 34·27 *grains.*

Synonyms: *Spiritus Nitro-ærius* (Mayow, 1674); *Dephlogisticated air* (Priestley, 1774); *Empyreal air* (Scheele, 1775); *Pure air* (Lavoisier, 1777); *Vital Air* (Condercet, 1777); *Oxygen* (Lavoisier, 1778, from ὀξὺς acid, and γεννάω, I generate).

History (*a*).—The earlier investigators devoted much attention to the nature of what they termed a calx, that is, the residue left after exposing a body to fire. *Rey* in 1630 thought a calx was formed by the fixation of air; *Boyle*, in 1660, regarded it as due to the fixation of heat; *Hooke* in 1670 again insisted that it was due to the fixation of air; whilst *Mayow* in 1674 said it was the fixation of a substance similar to what existed in saltpetre, which he termed the nitro-ærial spirit. This in great measure, anticipated Lavoisier's discoveries respecting combustion. His views were not, however, accepted, being opposed to the dominating theories of Beccher and Stahl.

(*b*) *Experimental facts.*—Priestley, on August 1, 1774, was experimenting on the calx of mercury (HgO) by heating it in a glass bulb over mercury with a burning glass, when he obtained oxygen, which he named, in accordance with the Stahlian theory, "Dephlogisticated air."

In 1775, Scheele, of Upsala, in Sweden, whilst examining the action of sulphuric acid on peroxide of manganese (pyrolusite) obtained a gas (oxygen) which he called "empyreal air," because of the energy with which it supported combustion.

Lavoisier (unfairly no doubt) claimed its discovery. He, however, was the first to explain the true nature of the red precipitate, from which Priestley originally prepared it, and showed that the process was an indirect means of obtaining oxygen from the air. Further, Lavoisier disputed the truth of the Stahlian theory, which taught

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that when any substance was burnt, it *gave out* "phlogiston," proving by actual experiment that the products of combustion (the calx) were heavier than the body burnt, and that therefore the body in burning could not have *given out* anything, but must have *taken in* something. The Stahlians, to meet this difficulty, imbued their phlogiston with the property of levity. Lavoisier then propounded his new theory of combustion, which was soon destined to overthrow the phlogistic theory. This was, "that combustion was the combination of a burning body with oxygen." He moreover rejected Priestley's name, "dephlogisticated air," and called it oxygen, or acid-begetter, inasmuch as he believed it to enter into the composition of all acids, and to constitute their acidifying principle.

Natural History.—Oxygen is the most abundant element in nature. Except in atmospheric air, however, it is always found in a combined state:—

(α.) *The Mineral Kingdom.*—The *solid crust* of the *earth* has three chief constituents—*carbonate of lime* ($CaCO_3$), of which $\frac{48}{100}$ is oxygen; *clay* (Al_2O_3), of which $\frac{48}{102}$ is oxygen; and *silica* (SiO_2), of which $\frac{32}{60}$ is oxygen. Thus about one-half of the solid crust of the earth is oxygen; (2) of the *water*, or liquid part, $\frac{8}{9}$ is oxygen; and (3) of the *air* or gaseous portion, $\frac{1}{5}$ by volume or $\frac{2}{9}$ by weight is oxygen.

(β.) *The Vegetable Kingdom.*—About $\frac{1}{4}$ of all growing vegetable matter is water, $\frac{8}{9}$ of which is oxygen; whilst of the solid part, which is principally cellulin ($C_6H_{10}O_5$) $\frac{80}{102}$, or about $\frac{1}{2}$ is oxygen.

(γ.) *The Animal Kingdom.*—Water constitutes about 75 per cent. of living animals, $\frac{8}{9}$ of which is oxygen. Of albuminous matters, about $\frac{23}{100}$, or nearly $\frac{1}{4}$ is oxygen.

Preparation.—(A.) *By the action of heat on certain metallic oxides and peroxides, as follows:—*

(1.) *Mercuric oxide* (HgO); Priestley, 1774; (216 grains produce 16 grains of oxygen or 46·7 cubic inches).—

$$2HgO = 2Hg + O_2.$$
Mercuric oxide = Mercury + Oxygen.
$$[2\mathbf{Hg}O = 2Hg + O_2].$$

(2.) *Red lead* (Pb_3O_4; triplumbic tetroxide); Priestley, 1774; (655 grains produce 16 grains of oxygen)—

$$2Pb_3O_4 = 6PbO + O_2.$$
Triplumbic tetroxide = Plumbic oxide (*Litharge*) + Oxygen.
$$[2\mathbf{Pb}Pb\text{o}''_2 = 6\mathbf{Pb}O + O_2].$$

(3.) *Manganic peroxide* (Pyrolusite); Scheele, 1775; (261 grains produce 32 grains of oxygen = 93.4 cubic inches)—

$$3MnO_2 = Mn_3O_4 + O_2.$$
Manganic peroxide = Trimanganic tetroxide + Oxygen.
$$[3\mathbf{Mn}O_2 = \mathbf{Mn}_3O_4 + O_2].$$

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(4.) *Baric peroxide;* Bousingault, 1851; (169 grains produce 16 grains of oxygen)—

$$2BaO_2 = 2BaO + O_2.$$
Baric peroxide = Baric oxide + Oxygen.
$$\mathbf{2Ba}O_2 = \mathbf{2Ba}O + O_2.$$

(5.) *Auric, argentic, platinic oxides.*

(B.) *By the action of heat on certain salts rich in oxygen*—

(1.) *Potassic chlorate* (Guy Lussac, 1814); (122·6 grains yield 48 grains of oxygen = 140·1 cubic inches).

The reaction occurs in two stages:—

(α.) A potassic perchlorate is first formed—

$$2KClO_3 = KCl + KClO_4 + O_2.$$
Potassic chlorate = Potassic chloride + Potassic perchlorate + Oxygen.

$$\left[2\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ko\end{matrix}\right. = KCl + \left\{\begin{matrix}\mathbf{O}\,Cl\\ O\\ \mathbf{O}Ko\end{matrix}\right. + O_2.\right]$$

(β.) The potassic perchlorate is then decomposed—

$$KClO_4 = KCl + 2O_2.$$
Potassic perchlorate = Potassic chloride + Oxygen.

$$\left[\left\{\begin{matrix}\mathbf{O}Cl\\ O\\ \mathbf{O}Ko\end{matrix}\right. = KCl + 2O_2.\right]$$

(2.) When potassic chlorate is mixed with manganic or with some other oxides it gives off its oxygen at a much lower temperature than when heated alone. According to the experiments of Wiederhold (Pogg Ann., cxvi., p. 171), confirmed by Baudrimont (Jr. Pharmacie, S. IV., xiv., p. 81 and 161) no perchlorate is formed under these conditions. (See Catalysis.)

(3.) *Zincic sulphate;* (Deville and Debray) (161 grains produce 16 grains of oxygen)—

$$2ZnSO_4 = 2ZnO + 2SO_2 + O_2.$$
Zincic Sulphate = Zincic oxide + Sulphurous anhydride + Oxygen.
$$[2\mathbf{S}O_2Zno'' = 2\mathbf{Zn}O + 2\mathbf{S}O_2 + O_2.]$$

(4.) *Alkaline nitrates*; (101 grains of KNO_3 produce 32 grains of oxygen = 93·4 cubic inches).

(5.) *Permanganates with superheated steam* (Marechal and Tessie du Mothay); (316·2 grains of steam and $KMnO_4$ produce 64 grains of oxygen)—

$$4K_2MnO_4 + 4H_2O = 8KHO + 2Mn_2O_3 + 3O_2.$$
Potassic permanganate + Steam = Potassic hydrate + Dimanganic trioxide + Oxygen.
$$[4\mathbf{Mn}O_2Ko_2 + 4OH_2 = 8OKH + 2\mathbf{Mn}_2O_3 + 3O_2.]$$

If a current of air be passed over the red hot residue, the permanganate will be reproduced.

(C.) *By heating certain compounds rich in oxygen with sulphuric acid.*

(1.) *Manganic peroxide and sulphuric acid;* (87 grains of MnO_2 produce 16 grains of oxygen)—

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$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$
Manganic peroxide + Sulphuric acid = Manganous sulphate + Water + Oxygen.
$$[2\mathbf{Mn}O_2 + 2\mathbf{S}O_2Ho_2 = 2\mathbf{S}O_2Mno'' + 2\mathbf{O}H_2 + O_2.]$$

(2.) *Potassic bichromate and sulphuric acid;* (295 grains of potassic bichromate produce 48 grains of oxygen)—

$$2K_2Cr_2O_7 + 8H_2SO_4 = 2K_2SO_4 + 2Cr_2 3SO_4 + 8H_2O + 3O_2.$$
Potassic bichromate + Sulphuric acid = Potassic sulphate + Chromic sulphate + Water + Oxygen.

$$2\left\{\begin{matrix}\mathbf{Cr}O_2Ko\\ O\\ \mathbf{Cr}O_2Ko\end{matrix}\right. + 8\mathbf{S}O_2Ho_2 = 2\mathbf{S}O_2Ko_2 + 2\mathbf{S}_3O_6{}'Cr'''_2O^{vi}) + 8\mathbf{O}H_2 + 3O_2.$$

(3.) *Plumbic peroxide and sulphuric acid;* (239 grains of plumbic peroxide produce 16 grains of oxygen)—

$$2PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O + O_2.$$
Plumbic peroxide + Sulphuric acid = Plumbic sulphate + Water + Oxygen.
$$[2\mathbf{Pb}O_2 + 2\mathbf{S}O_2Ho_2 = 2\mathbf{S}O_2Pbo'' + 2\mathbf{O}H_2 + O_2.]$$

(D.) *By the action of various oxides on hydric peroxide:*—

$$H_2O_2 + Ag_2O = H_2O + Ag_2 + O_2.$$
Hydric peroxide + Argentic oxide = Water + Silver + Oxygen.
$$\left[\left\{\begin{matrix}\mathbf{O}H\\ \mathbf{O}H\end{matrix}\right. + \mathbf{O}Ag_2 = \mathbf{O}H_2 + Ag_2 + O_2.\right]$$

(E.) *By the electrolysis of dilute sulphuric acid,* oxygen being evolved at the positive pole.

(F.) *By passing a mixture of steam and chlorine through a red hot tube:*—

$$2H_2O + 2Cl_2 = 4HCl + O_2.$$
Water + Chlorine = Hydrochloric acid + Oxygen.
$$[2\mathbf{O}H_2 + 2Cl_2 = 4HCl + O_2].$$

(G.) *By passing chlorine through a hot solution of sodic or potassic hydrate, containing a little chloride or nitrate of cobalt.* The chlorine converts the cobaltous hydrate into cobaltic hydrate, and subsequently the liquid effervesces and evolves oxygen. (Fleitman.)

(H.) *By dropping sulphuric acid into a red hot platinum retort:*—

$$2H_2SO_4 = 2H_2O + 2SO_2 + O_2.$$
Sulphuric acid = Water + Sulphurous anhydride + Oxygen.
$$[2\mathbf{S}O_2Ho_2 = 2\mathbf{O}H_2 + 2\mathbf{S}O_2 + \mathbf{O}_2.]$$

(I.) *By the action of the leaves of plants in sun-light on carbonic acid,* whereby the carbon is fixed, and oxygen set free ("Pharmaceutical Journal," July, 1873, p. 65).

Properties.—(*a.*) *Sensible.*—A colorless, odorless, tasteless gas.

(*b.*) *Physiological.*—If a rabbit be placed in pure oxygen at 75° F. (24° C.), it will live for about three weeks, eating voraciously all the time, but nevertheless becoming thin. The action of oxygen at 45° F. (7·2° C.), is to produce narcotism, and eventually death. When oxygen is cooled by a freezing mixture, it induces so intense a nar-

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cotism that operations may be performed under its influence. (Richardson.)

Compressed oxygen is "the most fearful poison known." The pure gas, at a pressure of 3½ atmospheres, or air at a pressure of 22 atmospheres, produces violent convulsions, simulating those of strychnia poisoning, and ultimately causing death. The arterial blood in these cases is found to contain about twice the quantity of oxygen that is normal. Further, compressed oxygen stops fermentation, and permanently destroys the power of the yeast. (Paul Bert.)

(*c.*) *Physical.*—Oxygen is 16 times heavier than hydrogen. Its experimental specific gravity is 1·1056, so that 100 cubic inches weigh 34·27 grains. Oxygen is a permanent gas, *i.e.*, it cannot be liquified, either by cold or by pressure. It refracts light less powerfully than any other gas (O=0·8, air=1). Oxygen is an electro-negative body, that is, it is attracted by the positive pole of the battery. It is the only gas that is magnetic (?), although its magnetism at best is but feeble, and is diminished by heat and increased by cold. Heat (as in the case of all other gases) expands it 0·3665 times its volume for every 1° C., and 0·002 times its volume for every 1° F. It is only slightly soluble in water; 100 volumes dissolve 3 to 4 volumes of oxygen.

(*d.*) *Chemical.*—Oxygen has no action either on litmus or on turmeric. It causes no precipitate with lime water. It forms red fumes of N_2O_4 with nitric oxide (N_2O_2). It is completely absorbed by a solution of pyrogallic acid in strong caustic potash. It supports combustion vigorously, but is not itself combustible;—hence Lavoisier's theory of combustion, that it was "*rapid oxidation.*"

Action on the metalloids.—Oxygen combines directly with all the non-metals except fluorine, with which it does not combine at all, and the other haloid bodies, with which it only combines indirectly, that is, through the intervention of a third body. It combines, however, with none of the metalloids *at ordinary temperatures*, except with phosphorus, in which case the energy of oxidation may be so intense that combustion results. If carbon, sulphur, or phosphorus be burnt in oxygen, bodies are formed (viz., CO_2, SO_2, and P_2O_5), which, when dissolved in water, redden litmus. All the non-metals, except hydrogen and fluorine, form, by their union with oxygen, anhydrides, which, when dissolved in water, constitute acids. Hence, Lavoisier taught "that oxygen was the acidifying principle of all acids," a theory we now know to be incorrect.

Action on the metals.—Oxygen combines directly, under certain conditions, with all the metals, except gold, silver, and platinum (Noble metals). Combination, however, does not usually occur at ordinary temperatures, except in the case of a few metals, such as sodium, potassium, barium, strontium, and calcium, and in some other cases where the metals have been reduced to a state of minute subdivision (pyrophoric). Only a very moderate heat, however, is usually re-

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quired to effect a union. Iron, lead, etc., undergo superficial oxidation in the air at common temperatures, but this is dependent on certain circumstances that favor oxidation, such as the presence of moisture, carbonic anhydride, etc.

When a metal combines with oxygen, it generally forms what is called a *base*, that is, "*a compound body capable completely or in part of neutralizing an acid.*" The compounds, formed by the union of the alkaline metals with oxygen, are called alkalies or alkaline bases, as, *e.g.*, sodic oxide (Na_2O) potassic oxide (K_2O), etc. These bodies are very soluble in water. The other metals also form bases with oxygen, but they are practically insoluble in water; nevertheless they are capable either entirely or in part of neutralizing acids (ZnO—Fe_2O_3). No non-metal ever forms a base by its union with oxygen, although some metals form anhydrides by such combination. This anhydride is always the highest oxide that the metal is capable of forming, as *e.g.*, stannic anhydride, SnO_2—antimonic anhydride, Sb_2O_5, etc. There are certain oxides that are neither acids nor bases, and are known as "*indifferent oxides*" from their similarity to salts. Such, for example, are water (H_2O), manganic peroxide (MnO_2), etc.

Various methods have been devised for estimating the quantity of free oxygen present in a mixed gas. In most cases the oxygen is removed by absorbent agents, such as moist phosphorus or certain moist metals (iron, lead, etc.); certain low oxides, such as FeO or N_2O_2 (Priestley); or a mixture of the last two bodies (Davy); the ammoniochloride of copper (Graham); pyrogallic acid dissolved in an alkaline solution (Liebig); red-hot copper or iron (Dumas); cuprous oxide (Cu_2O) in ammonia ("Chemical News," vol. xxxiii., p. 5); also by exploding the gas with hydrogen. These methods of estimating oxygen will be referred to under the analysis of air.

Allotropic Oxygen: Ozone (ὄζω, I smell).

Molecular weight=48. *Molecular volume* $\square$. 1 *litre weighs* 24 *criths* (0·0896 *grm.* × 24) 2·1504.

History.—*Von Marum* (1780) noticed that air or oxygen, through which electric sparks had been passed, possessed a peculiar odor, and rapidly tarnished quicksilver. Schönbein, of Basle, in 1840, showed that this peculiar smelling gas was developed by exposing moist phosphorus to air. Since 1840 ozone has been further examined by Marignac, De la Rive, Fremy, Becquerel, Andrews, etc.

Natural History (See OZONE under AIR).

Nature of Ozone.—Schönbein, in the first instance, regarded ozone as a peroxide of hydrogen (H_2O_2, or in old formula HO_2); Baumert and Williamson fixed H_2O_3 as its composition, because water and oxygen, as they supposed, were formed by its decomposition: ($H_2O_3 = H_2O + O_2$). Berzelius, Marchand, Erdmann, Marignac, De la Rive, Fremy, Becquerel, and Andrews afterwards showed that pure *dry* oxygen can be ozonized, whilst Andrews proved that with proper precautions no

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water results from its decomposition. Schönbein afterwards regarded ozone as permanently negative oxygen ($\bar{O}$), there being, as he thought, a permanently positive oxygen ($\overset{+}{O}$) (antozone), a body which has not as yet been obtained in a free state (see page 63).

Chemists are now tolerably agreed that ozone is an allotropic oxygen, where three volumes are condensed into two, one of the volumes being in a different polar condition to the other two ($\overset{-+-}{\underset{\sim\sim}{OOO}}$=two volumes.) This view is confirmed by the observation of Andrews that, when ozone is absorbed by mercury or by potassic iodide, the volume of the gas is not affected.

$$\underset{\text{2 vols. of Ozone.}}{\overset{-+-}{\underset{\sim\sim}{OOO}}} + Hg = HgO + \underset{\text{2 vols. of Common O.}}{\overset{+-}{\underset{\sim\sim}{OO}}}$$

Preparation.—Ozone, however prepared, always contains a large admixture of air or oxygen. The following are some of the methods by which it may be obtained:—

(1.) By *electrical agency*. The silent passage of electricity through damp oxygen, is the method best adapted for its generation. A small induction spark, or the brush from the electrical machine, may also be employed, but the long spark from the coil, on account of its high temperature, destroys the ozone as fast as it is generated. Various ozonizers have been invented, in order to secure this silent passage of electricity through oxygen. That of *Houzeau* consists of a glass tube filled with oxygen, a platinum wire being placed in the centre of the tube, attached to one terminal of an induction-coil, whilst a second wire is wound round the glass tube and attached to the other terminal. *Siemen's ozoniser* consists of two glass tubes, one placed inside but separate from the other by a small interval, through which a stream of oxygen may be continuously passed. The internal tube has its inner surface, and the external tube its outer surface, covered with tin-foil. When these are connected with different poles of the coil, a silent discharge takes place between them, whereby the ozonization of the intermediate oxygen is effected. By means of these ozonizers, 60 to 120 milligrammes of ozone per litre of oxygen may be obtained.

(2.) By the *electrolysis of dilute sulphuric acid*. The oxygen which is set free at the positive pole by the electrolysis of dilute sulphuric acid contains about $\frac{1}{260}$ part of its volume of ozone, *i.e.*, about 3 to 5 milligrammes per litre. The water mixed with the acid should be free from all organic or other oxidizable matters, and the presence of a little bichromate of potash in solution is said to assist its formation. (Baumert.)

(3.) By *slow combustion* (Eremacausis): (a) *of phosphorus in moist air* (Schönbein). The phosphorus employed should be freshly scraped, and kept at a temperature of from 70° to 90° F. (21° to 32° C.) It

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should not be allowed to act on the same air for more than an hour, otherwise the ozone first generated will be decomposed. The action is more complete if the air in the vessel be slightly rarefied, the best effects being produced by employing a mixture of hydrogen and oxygen in the place of air. (β.) By the *slow combustion of ether and volatile oils.* When the combustion of ether is effected by glowing platinum, or by placing a hot glass rod in a bottle filled with the vapour, ozone is produced, together with certain acid vapours. Aromatic plants and flowers are also said to generate ozone (Mantegazza), although the recent experiments of Kingsett indicate that hydroxyl, and not ozone, is generated under these circumstances.

(4.) By the *rapid combustion of all bodies containing hydrogen.* The generation of ozone under these conditions is supposed to be due to the hydrogen molecule combining with a half molecule of oxygen (α), leaving the other atom of oxygen free to combine with a second oxygen molecule to form ozone (β). Thus—

$$(\alpha.)\ H_2 + O_2 = H_2O + O\ ;\quad (\beta,)\ O + O_2 = O_3.$$

Ozone is not formed by the combustion of carbon, inasmuch as carbon combines not with half molecules of oxygen (O), but with complete molecules (O_2). (Thau.)

(5.) By the *action of oxygen on fine particles and on large surfaces.* When lead pyrophorus is exposed to the air, it catches fire spontaneously, owing to the generation of ozone, by the action of air on the finely-divided metallic particles.* Similarly, when phosphorus is dissolved in bisulphide of carbon, and the solvent allowed to evaporate, the finely-divided phosphorus fires spontaneously.

(6.) By *nascent action.* The intense activity of nascent oxygen, it is thought, may be due to the gas being ozonic. Probably the oxygen set free by plants from the decomposition of carbonic anhydride is also ozonic. (De Lucca, "Pharmaceutical Journal," July, 1873, p. 65.) Possibly to this may be traced the bleaching action of morning dew.

Properties of Ozone.—(α.) *Sensible.* A colorless gas having a peculiar phosphorus-like odor (ὄζω, I smell).

(β.)—*Physiological.* Its special action in respiration will be discussed further on (page 64). It acts as an intense irritant to the eyes and nose, and rapidly proves fatal to animal life. (Thénard and Schönbein.)

(γ.) *Physical.*—Ozone consists of 3 volumes of oxygen condensed into 2 volumes; hence its density must be 1½ times the density of common oxygen; 1 litre, therefore weighs (8 × 3) 24 criths (see page 35). It decomposes slowly in the presence of moisture at 212° F. (100° C.), but decomposes instantly at a temperature of from 450° to 500° F. (232° C. to 260° C.), the ozone becoming ordinary oxygen. Ozone is only slightly soluble in water. At 32° F. (0° C.) 100 volumes of water dissolves ½ volume of ozone (Carius). It is not soluble in solutions of acids or alkalies.

* Possibly this action may be due to the carbon present absorbing oxygen, and so bringing it within the sphere of affinity.

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(δ.) *Chemical.*—Ozone is a powerful oxidiser. This action depends on its desire to throw off one of its oxygen atoms, and so return to the condition of ordinary oxygen. It bleaches litmus, and is almost as powerful a supporter of combustion as ordinary oxygen.

(1.) *Action on the Non-metallic Elements.*—These are as a whole but little and but slowly affected by it. It rapidly oxidizes the compounds of hydrogen with phosphorus, sulphur, and selenium.

(2.) *Action on Metals.*—None of the metals, except mercury, are affected by dry ozone, whilst in the presence of moisture, nearly all the metals (except gold and platinum) are oxidized by it. Even metallic silver is converted into a peroxide. It is to be noted that, under these circumstances, no contraction of the gas results, the ozone returning from the triatomic to the diatomic condition of ordinary oxygen.

(3.) *Action on Mineral Compounds.*—Ozone converts the protoxides and protosalts of lead, tin, iron, manganese, etc., into peroxides and persalts. Some peroxides decompose ozone, and are themselves, at the same time, partially reduced. Thus the peroxides of copper, manganese, and barium, etc., exhibit this catalytic action on ozone:—

$$BaO_2 + O_3 = BaO + 2O_2.$$

The sulphides and selenides are also oxidized by it. It decomposes iodide of potassium, iodine being set free.

(4.) *Action on Organic Matter and on Organic Compounds.*—Organic bodies generally are speedily oxidized by ozone. It bleaches indigo, converting it into *isatin;* tincture of guiacum is turned green by it; cork and caoutchouc are speedily acted upon. Putrid flesh is deodorized. Strychnia and aniline assume various tints under its action. It is absorbed by turpentine. It has no action on paraffin, which may therefore be used for joining apparatus used in its generation, and in experiments upon it.

Special Tests for Ozone.—(1.) White bibulous paper soaked in a solution of 1 part of potassic iodide, 5 parts of starch, and 100 parts of water, constitutes the common ozone test-paper. Ozone displaces the iodine from its combination, the iodine thus set free blueing the starch. For determining the presence of ozone in the air, Schönbein employs *moist* ozone papers, whilst Moffatt prefers them *dry*. The fallacies to this as a test for ozone, are the presence in the air of chlorine or of the oxides of nitrogen.

(2.) *Houzeau's Ozonometer* consists of neutral litmus paper, soaked in a dilute solution of potassic iodide, the potash set free by the ozone turning the paper blue. A piece of the litmus paper without iodide, is also exposed to the air at the same time, a comparison of the two papers indicating how far the action on the iodide paper may be due to ammonia in the air, and not to the action of ozone.

(3.) A solution of *sulphate of manganese* is turned brown by ozone.

(4.) A colorless solution of a *protosalt of thallium* is turned yellow by ozone, but not by the oxides of nitrogen ("Intellectual Observer,' 1867, p. 399).

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Quantitative Determination.—This is made either (1) by means of a weighed quantity of dry mercury, which rapidly absorbs ozone, or (2) by estimating the amount of iodine liberated in a solution of potassic iodide of known strength, a little hydrochloric acid being added to prevent the absorption of carbonic acid :—

$$O_3 + 2KI + H_2O = O_2 + I + 2KHO.$$

Antozone.

Schönbein first, and afterwards Brodie, directed attention to the fact that oxygen appears to exist in certain compounds, not only in a state different from, but actually antagonistic to, ozone. Schönbein termed this form of oxygen, *antozone*. Brodie was of opinion that the difference between ozone and antozone depended on the oxygen in the two cases being in different polar conditions, its polarity being determined by the body with which it was associated (Odling, p. 125).

For example; (α.) The oxygen existing in *peroxide of manganese* (MnO_2), in *peroxide of lead* (PbO_2), in *chromic acid* (H_2CrO_4), and in *manganic acid* ($HMnO_4$), was regarded as ozonic, for in a nascent state it was found to color strychnia and guiacum ; whereas—

(β.) The nascent oxygen evolved from the *peroxides of barium, of strontium, of calcium*, and *of hydrogen*, on the contrary, was incapable of coloring strychnia or tincture of guiacum. And, further, the oxygen obtained from this latter series seemed to be in some respects absolutely antagonistic to, and destructive of, the ozone obtained from the former series, combining with it to form common oxygen. Thus, peroxide of hydrogen is decomposed by the oxides of mercury, silver, gold, or platinum, these latter oxides being themselves reduced during the process, whilst ozone was found to decompose *peroxide of hydrogen* leaving water, and *peroxide of barium* (BaO_2) leaving BaO, and common oxygen in each case.

These facts suggested the notion that the oxygen present in these bodies must exist in different polar or electrical states, and that the antagonism was due to the power of the one to neutralize the other. Thus—

(1.) (α.) *Ozone and peroxide of hydrogen.*

$\overset{-+-}{OOO}$	+	$H_2\overset{+\ -+}{OO}$	=	$2\overset{-+}{OO}$	+	$H_2\overset{+\ -}{O}$
Ozone	+	Peroxide of hydrogen	=	Common oxygen	+	Water.

(β.) *Ozone and peroxide of barium.*

$\overset{-+-}{OOO}$	+	$Ba\overset{+\ -+}{OO}$	=	$2\overset{-+}{OO}$	+	$Ba\overset{+\ -}{O}$
Ozone	+	Baric peroxide	=	Common oxygen	+	Baric oxide.

(2.) (α.) *Peroxide of hydrogen and peroxide of manganese.*

$Mn\overset{+\ --}{OO}$	+	$H_2\overset{+\ -+}{OO}$	=	$Mn\overset{+\ -}{O}$	+	$H_2\overset{+\ --}{O}$	+	$\overset{+-}{OO}$
Peroxide of manganese	+	Peroxide of hydrogen	=	Manganese oxide	+	Water	+	Common oxygen.

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(β.) *Peroxide of hydrogen and the oxides of the noble metals.*

$\overset{+}{Ag}\overset{-}{Ag}\overset{-}{O}$	+	$\overset{+}{H}_2\overset{-}{O}\overset{+}{O}$	=	$\overset{+}{Ag}\overset{-}{Ag}$	+	$\overset{+}{H}_2\overset{-}{O}$	+	$\overset{+}{O}\overset{-}{O}$
Argentic oxide	+	Peroxide of hydrogen	=	Silver	+	Water	+	Common oxygen.

From this it was inferred that oxygen was capable of existing in at least three states, which were represented as follows—

(1.) *Common oxygen:* $\overset{=}{O}$ or $\overset{+-}{O}\overset{+-}{O}$;

(2.) *Ozonic oxygen:* $\overset{-}{O}$ or $\overset{+-}{O}\overset{+-}{O}+\overset{-}{O} = \overset{-+-}{O}\overset{+-}{O}\overset{-}{O}$;

(3.) *Antozonic oxygen:* $\overset{+}{O}$ or $\overset{+-}{O}\overset{+-}{O}+\overset{+}{O} = \overset{+-+}{O}\overset{+-}{O}\overset{+}{O}$.

The recent researches of V. Babo, Weltzien, etc., have, however, proved beyond a doubt that this peculiar body, called antozone by Schönbein, is, after all, merely peroxide of hydrogen (p. 209).

Uses of Oxygen.—(α.) *In nature* oxygen acts as the great burner up of dead organic matter. We see *eremacausis* or slow oxidation taking place in the decay of wood (dry oxidation), in the formation of *humus and peat* (wet oxidation), and in the change of wood into coal (wet and imperfect oxidation). In *nitrification* we see the action of oxygen producing nitre. Oxygen effects the *resinification* of the fixed and volatile oils, illustrated in the drying of paint, in the occasional firing of greasy rags, and more generally in the formation of resins. The *acetification* of alcohol, again, is an oxidizing action: thus—

C_2H_6O	+	O_2	=	$C_2H_4O_2$	+	H_2O
Alcohol	+	Oxygen	=	Acetic acid	+	Water.

Respiration.

By the act of respiration the oxidation of tissue is effected. This is a process common to all animals. Oxygen must be brought, by some means or another, into contact with the blood, and by it with the body generally. In some animals we find for this purpose a minute series of tubes, along which air is conveyed through the system. In fish, the water containing oxygen in solution, passes through the gills, and coming into contact with a fine membrane, upon the opposite side of which the blood of the animal circulates, there occurs a free interchange of gases. In some animals, as in frogs, respiration is, in great part (and in the higher animals in a lesser degree), cutaneous transpiration; whilst in animals generally the lungs constitute the principal machinery for effecting the proper oxygenation of the blood. In respiration the changes produced are threefold; (1) *a visible* or *color change;* (2) *a physical* or *heat change,* resulting from chemical combination; and (3) *a chemical change.* The facts of respiration were collected slowly; Mayow (1674) proved the taking in by the lungs of something present in the air; Black (1757) proved the return of something to the air during exhalation; whilst Lavoisier proved that the active gas taken in by the lungs, was oxygen, and that the gas returned was carbonic anhydride. He was further of opinion that the animal heat was the result of a process

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of combustion, the union of carbon and oxygen. But he noted that the carbonic anhydride given back to the air, only accounted for a portion of the oxygen taken from the air.* Hence arose a theory of diffusion, which regarded respiration as a purely physical act. This may be stated as follows:—The venous blood, rich in carbonic acid but poor in oxygen, passes into the minute pulmonic capillaries, external to which is a mixed gas (the air), containing very little carbonic acid, but rich in oxygen; hence an interchange of gases takes place to establish equilibrium. More recent experiments, however, have shown that breathing is not merely a physical, but a chemical act. In the red blood-corpuscles a compound exists called "hæmoglobin." This body has a purple color in venous blood, but is capable of combining chemically with oxygen to form a vermilion red body called "oxyhæmoglobin," the coloring matter of arterial blood. The active agent in respiration is this hæmoglobin, a body remarkable for the ease with which it both combines with, and also delivers up, oxygen. Asphyxia means the non-oxygenation of the purple hæmoglobin. Other gases, such as carbonic oxide, are also capable of combining with it, forming "*carbonic oxide hæmoglobin*," which is of a like red color to oxyhæmoglobin, but, unlike it, in that, when once formed, the hæmoglobin cannot part with the carbonic oxide, in the same way that it can with oxygen. Hence the cause of death in poisoning by this gas.

Experiments (some teach) have shown that the blood corpuscles possess the power of ozonizing the oxygen inhaled, peroxide of hydrogen being formed by its combination with water. This compound is again decomposed into water and oxygen, which oxygen in its nascent state serves for the purposes of oxidation. It is certain that both blood and hæmoglobin have the power of setting free the oxygen absorbed by oil of turpentine, and that blood globules act similarly on peroxide of hydrogen. The nascent oxygen thus evolved is capable of acting on such bodies as potassic iodide and starch, tincture of guiacum, etc. In fact, Schönbein taught that the function of the blood corpuscles was the chemical excitement of the oxygen of the respired air. If hæmoglobin be mixed with alcohol or heated to 212° F., it then loses the power of decomposing the peroxide. Thus it is held that there is perpetually going on, in the animal organism, this formation and destruction of ozone and peroxide of hydrogen. The solution of the corpuscles and their alteration into other products is believed to be due to the ozone. These products have no longer any plastic property, and in this way Schmidt believes that the fluidity of the blood is maintained. (Schönbein, Schmidt, Schreiber, etc.)

The quantity of oxygen required for respiration is important. It

* *Herbivorous* animals are said to exhale carbonic acid in volume equal to the oxygen taken in, but carnivorous animals exhale a volume of carbonic acid 40 per cent. less than the inhaled oxygen.

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varies with sex, age, diet, exercise, etc. The following facts are important:—

I. *The Carbon daily consumed as food, and daily evolved as Carbonic Acid.* (Dr. E. Smith.)

Adult Man.	Carbon consumed in diet daily.		Carbon evolved by lungs daily as CO_2.	
	ozs.	grains.	ozs.	grains.
In idleness	8·72	3815	7·85	3434
With ordinary labour ..	13·00	5688	9·11	3985
With active work	15·60	6825	12·90	5644

The 3985 grains of carbon evolved per day from the lungs by a man in ordinary work is equivalent per hour to about 1240 cubic inches of carbonic acid.

Carbon consumed per hour by males (Andral and Gavarret).

Up to 8 years of age	77	grains per hour.
From 8 to 15	133	,, ,,
,, 15 to 20	175	,, ,,
,, 20 to 40	185	,, ,,
,, 40 to 60	155	,, ,,
,, 60 and over	95	,, ,,

Females consume somewhat less, viz., 98 grains per hour from 15 to 40.

II. *The oxygen daily consumed by the food taken by an average man.*

(The following results are the mean of the observations of Dumas, Liebig, Regnault, Lassaigne, Scharling, and Smith):—

	ozs.	cubic feet.
Oxygen consumed by the 9 ozs. of the carbon of food ..	24	= 17·73
,, ,, ,, ½ oz. ,, hydrogen ,, ..	4	= 2·95
Total of oxygen consumed daily	28	= 20·68

This is at the rate per hour of

1489 cubic inches of oxygen; or
7445 ,, ,, of air.

III. Normal air contains 0·04 per cent. (or 4 parts in 10,000) of carbonic acid. Air containing 4 per cent. of carbonic acid (the quantity present in expired air) is perfectly irrespirable; air containing 1 per cent. of carbonic acid is extremely distressing; air containing 0·1 per cent. may be regarded as polluted.

IV. It follows that the quantity of air used *per hour* (7445 cubic inches) *plus* that vitiated by the 1240 cubic inches of carbonic acid expired, must be—

At 4 per cent. of CO_2	38,445 cub. in.	= 22·22 cub. ft.
At 1 ,, ,,	131,445 ,,	= 76·08 ,,
At 0·1 ,, ,,	1,247,445 ,,	=723·64 ,,

V. The quantity of air required for respiration by an ordinary man, is equal to that contained in a room 9 ft. square and 9 ft. high, renewed every hour, whilst for good breathing it should be renewed every half-hour. When, therefore, we fix 300 cubic feet as the space per head in sleeping-rooms, it is manifest that this must be regarded as the very minimum, and implies thorough ventilation.

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VI. In these calculations the carbonic acid from the lungs is the only product considered. There is also, however, the carbonic acid given off from the skin, etc., which should also be taken into account.

It may be noted that a horse consumes about 13 times as much oxygen as a man; that is, he requires about 19,000 cubic inches of oxygen, and 95,000 cubic inches of air, per hour.

(a.) *Use of oxygen as an agent of combustion:*

The following table shows the quantity of oxygen consumed, the CO_2 produced, and the air vitiated by the combustion of 1 lb. of the following substances—

One pound of	Cubic ft. of Oxygen consumed.	Cubic ft. of Air consumed.	Cubic ft. of Carbonic Acid (CO_2) produced	Cubic ft. of Air vitiated (that is CO_2 =1 per ct.)	Heat produced in lbs. of water raised 10°F.
Newcastle Coal	30·15	150·75	25·62	2713	1159
Dry Wood	15·85	79·25	15·30	1609	676
Dry Turf	17·15	85·75	16·51	1737	579
Coke	28·14	140·70	28·88	3129	1255
Charcoal	31·26	156·30	31·11	3267	1409
Camphine	38·90	194·5	27·8	2974·5	1957
Benzol	36·3	181·5	29·1	3091·5	1820
Spermaceti	37·0	185·0	25·2	2705·0	1759
Wax	37·7	188·5	25·6	2748·5	1581
Stearic Acid	34·6	173·0	24·0	2573·0	1705
Stearin	34·4	172·0	24·2	2592·0	1800
Paraffin	40·5	202·5	27·0	2902·5	2133
Paraffin Oil	40·5	202·5	27·0	2902·5	2133
Rape Oil	38·7	193·5	24·3	2623·5	1775
Sperm Oil	38·7	193·5	24·3	2623·5	1775
1 cubic foot of common coal gas = 14 candles	1·17	5·85	0·55	60·55	65
1 cubic foot of cannel coal gas = 20 candles	1·56	7·80	0·83	90·80	76

The following table shows the oxygen consumed, the carbonic acid produced, and the air vitiated, by the combustion of certain bodies, burnt so as to give the light of 12 standard sperm candles, each candle burning at the rate of 120 grains per hour each:—

Burnt to give light of 12 candles = to 120 grains per hour.	Cubic ft. of Oxygen consumed.	Cubic ft. of Air consumed.	Cubic ft. of Carbonic Acid (CO_2) produced.	Cubic ft. of Air vitiated (that is CO_2 =1 per ct.)	Heat produced in lbs. of water raised 10°F.
Cannel Gas	3·30	16·50	2·01	217·50	195·0
Common Gas	5·45	27·25	3·21	348·25	278·6
Sperm Oil	4·75	23·75	3·33	356·75	233·5
Benzole	4·46	22·30	3·54	376·30	232·6
Paraffin	6·81	34·05	4·50	484·05	361·9
Camphine	6·65	33·25	4·77	510·25	325·1
Sperm Candles	7·57	37·85	5·77	614·85	351·7
Wax „	8·41	42·05	5·90	632·25	383·1
Stearic „	8·82	44·10	6·25	669·10	374·7
Tallow „	12·00	60·00	8·73	933·00	505·4

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It would thus appear that, of the substances named, cannel gas vitiates air the least, and tallow candles the most, and that the order of their vitiating effect, is also very nearly the order of their heating effects.

Regnault has shown that the same heat which will raise 1 lb. of water 1° F., will raise 49 cubic feet of air (= 3·6 lbs.) 1° F.; or, again, that the heat that will raise 1 cubic foot of water (=62·23 lbs.) 1° F., will raise 3,054 cubic feet of air (= 233·71 lbs.) to the same extent.

(β.) *Use of oxygen as an oxidizing body.*—Endless illustrations of this action might be given.

(γ.) *Use of oxygen in medicine.*—"Searle's oxygenated water," and "Gardner's peroxide of hydrogen," have been used in medicine, but their efficacy is doubtful.

Lastly, we note that the regular supply of oxygen in the air is maintained by plant-life, the carbon being retained by the plant, and the oxygen evolved for the animal. Thus—

$$12CO_2 + 11H_2O = \underset{\text{Sugar.}}{C_{12}H_{22}O_{11}} + 12O_2.$$

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CHAPTER IV.

THE HALOGENS OR HALOID ELEMENTS.

FLUORINE. CHLORINE: Compounds of Chlorine and Oxygen—Hypochlorous anhydride—Hypochlorous acid—Chlorous anhydride—Chlorous acid—Chloric peroxide—Chloric acid—Perchloric acid. BROMINE: Compounds of Bromine with Oxygen and Chlorine. IODINE: Compounds of Iodine and Oxygen—Iodic acid—Periodic acid—Compounds of Iodine and Chlorine—Generalization on the Halogens.

FLUORINE (F = 19).

Atomic weight, 19. *Atomicity monad* (′) (*as in* HF). *Relative weight* (H=1)19. *Specific gravity* (*Air* = 1), (*theoretical* 0·0693 × 19) 1·3186. 1 *litre weighs* 19 *criths* (0·0896 × 19) = 1·7024 *grms.* 100 *cubic inches weigh* (*estimated*) 40·87 *grains.*

Synonyms.—*Fluoric radical* (Berzelius); *Fluoricum*; *Fluorine* (Sir H. Davy, from Fluor Spar).

History.—Davy in 1808 suspected hydrofluoric acid to be a compound of oxygen with a combustible base. In 1812 and 1813 he obtained by the electrolysis of the acid, hydrogen at the negative pole, and free fluorine at the positive pole. He was unable, however, to collect the fluorine, owing to its intense action on the vessels used in the experiment. The Messrs. Knox, of Dublin, in 1836, and Davy, in 1840, obtained fluorine by electrolysing hydrofluoric acid in fluor spar bottles. In 1858 Phipson is also stated to have obtained it, by heating hydrofluoric with nitric acid. It has been examined at different times by Fremy, Baudrimont, Kammerer, and by other chemists.

Natural History.—It is never found in nature in a free state. (α.) *In the mineral kingdom* it is tolerably abundant, both as fluor or Derbyshire spar (CaF_2), and as cryolite ($6NaF,Al_2F_6$). It exists also as a fluoride of cerium, and is found in certain minerals, such as wavellite, mica, fluor, apatite, topaz, etc. It is also present in sea and in many mineral waters. (β.) *In the vegetable kingdom* it occurs in numerous plants, and particularly in the siliceous stems of grasses. (γ.) *In the animal kingdom* it is found in the teeth, bones, milk, blood, urine, etc. Bone contains about 2 per cent. of fluoride of calcium (CaF_2).

Preparation.—1. By the electrolysis of hydrofluoric acid in fluor spar vessels. (Davy and the Messrs. Knox.)

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2. By the action of sulphuric acid on a mixture of peroxide of manganese and fluor spar.

$$2H_2SO_4 + MnO_2 + CaF_2 = MnSO_4 + CaSO_4 + 2H_2O + F_2.$$

Sulphuric acid + Manganic peroxide + Calcic fluoride = Manganic sulphate + Calcic sulphate + Water + Fluorine

$$[2SO_2Ho_2 + MnO_2 + CaF_2 = SO_2Mno'' + SO_2Cao'' + 2OH_2 + F_2.]$$

3. By electrolysing fused potassic fluoride. (Fremy.)

4. By heating for 24 hours, at 170° F. (77° C.), in an hermetically-sealed tube in which the air has been previously displaced by iodine vapor, a mixture of iodine with an excess of argentic fluoride, an iodide of silver and a fluoride of iodine (IF_5) being formed. (Kammerer.)

Properties.—(α.) *Sensible.* A gas said to have a yellow color, like chlorine, but that produced by Kammerer's process is colorless. Its odor is very powerful.

(β.) *Physiological.*—Its action on the animal body is very deleterious and irritating.

(γ.) *Physical.*—It has an estimated specific gravity of 1·3186; 100 cubic inches should weigh, therefore, 40·87 grains, and a litre 1·7024 grms.

(δ.) *Chemical.*—It combines with every known element, except oxygen. Its action on all bodies, especially on silicon (glass), and on the metals, is intensely energetic. The difficulty of collecting it is so great, that an accurate study of its properties is rendered almost impossible. It is said to be absorbed by caustic potash, potassic fluoride and hydric peroxide being formed ($2KHO + F_2 = 2KF + H_2O_2$). It has no special uses.

CHLORINE (Cl = 35·5).

Atomic weight, 35·5. *Molecular weight*, 71. *Molecular volume*, |_|_|. *Atomicity monad* (') (HCl). *Relative weight* (H=1) 35·5. *Specific gravity* (*Air* = 1) *observed*, 2·47; *theoretic* (0·0693 × 35·5), 2·4601. 1 *litre weighs* 35·5 *criths* (0·0896 *grm.* × 35·5) = 3·1808 *grms.* 100 *cubic inches, at* 60° *Fah. and* 30 *B.P., weigh* 76·3 *grains.*

Synonyms. — *Dephlogisticated marine acid* (Scheele); *oxygenated muriatic acid* (Berthollet); *oxymuriatic acid* (Kirwan and Pearson); *muriaticum*, or *muriatic radical*, (Berzelius); *Chlorine* (Davy, from χλωρὸς, green).

History.—Discovered by Scheele (1774) when acting on peroxide of manganese (pyrolusite) with hydrochloric acid. It was further examined by Berthollet (1785), and named by him "oxygenated muriatic acid," because, when placed in sunlight, he found that the *moist* gas split up, as he supposed, into oxygen and muriatic acid. Thénard (1809) showed, however, that it was impossible to effect this decomposition with *dry* chlorine, whilst Davy (1810) further proved its elementary nature.

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Natural History.—It is never found free in nature. (*a.*) *In the mineral kingdom,* it occurs in combination with sodium and with other metals, in salt mines, in sea water, and in various horn-minerals, such as the chlorides of lead, silver, mercury, etc. In volcanic districts it is found combined with hydrogen. (*β.*) *In the vegetable kingdom,* it is not an abundant element; but in (*γ*) *the animal kingdom,* it is found in all secretions. Its absence in the urine in pneumonia, constitutes a peculiarity of that disease.

Preparation.—The first process described is the common laboratory process, and the process of the B. P. for the preparation of liq. chlori. The first three are trade processes, the second being that commonly used in the manufacture of chloride of lime.

(1.) By heating a mixture of manganic peroxide and hydrochloric acid. (Scheele.) The reaction takes place in two stages:—

(*a.*)
$$MnO_2 + 4HCl = MnCl_4 + 2H_2O.$$
Manganic peroxide + Hydrochloric acid = Manganic tetrachloride + Water.
$$[\mathbf{Mn}O_2 + 4HCl = \mathbf{Mn}Cl_4 + 2\mathbf{O}H_2]$$

(*β.*)
$$MnCl_4 = MnCl_2 + Cl_2.$$
Manganic tetrachloride = Manganous chloride + Chlorine.
$$[\mathbf{Mn}Cl_4 = \mathbf{Mn}Cl_2 + Cl_2].$$

In *Weldon's* process, (which is employed in dealing with the "still liquors" of bleaching-powder factories), the $MnCl_2$ formed as above, is decomposed by lime:—

$$MnCl_2 + CaO = MnO + CaCl_2.$$

This MnO is then mixed with more lime, and air blown through the mixture, whereby the MnO is converted into MnO_2, which may be again used for generating chlorine with hydrochloric acid.

It has been suggested by Schlösing to prepare chlorine by heating the peroxide of manganese with a mixture of nitric and hydrochloric acids. Chlorine is evolved, whilst the manganous nitrate formed, yields, when heated, MnO_2 and nitric acid, which may be again used to decompose fresh hydrochloric acid.

(2.) By heating a mixture of sulphuric acid with manganic peroxide and common salt. In this process the whole of the chlorine present is liberated.

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2.$$
Sodic chloride + Manganic peroxide + Sulphuric acid = Sodic sulphate + Manganic sulphate + Water + Chlorine.
$$[2NaCl + \mathbf{Mn}O_2 + 2\mathbf{S}O_2Ho_2 = \mathbf{S}O_2Nao_2 + \mathbf{S}O_2Mno'' + 2\mathbf{O}H_2 + Cl_2.]$$

(3.) By passing air and hydrochloric acid gas through red-hot tubes. (Oxland.)

$$2HCl + Air\ (O \text{ and } N_4) = H_2O + Cl_2 + N_4.$$

This process has been improved by Deacon ("Journ. Chem. Soc.," x., 725), who passes the mixed air and hydrochloric acid gas over fire-bricks, which are first soaked in a solution of cupric sulphate or of

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cupric chloride, and afterwards dried. The cuprous chloride first becomes cupric chloride (α), which, by an increased heat, gives up its chlorine, and again becomes cuprous chloride (β). Thus—

(α.) $Cu_2Cl_2 + O + 2HCl = 2CuCl_2 + H_2O$.
Cuprous chloride + Oxygen + Hydrochloric acid = Cupric chloride + Water.

(β.) $2CuCl_2 = Cu_2Cl_2 + Cl_2$.
Cupric chloride = Cuprous chloride + Chlorine.

It will be remarked that in this process, the chlorine is mixed with twice its bulk of nitrogen, but for trade purposes this admixture is of no importance.

(4.) By the action of heat on hydrochloric acid and potassic bichromate. (Rogers.)

$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$.
Potassic bichromate + Hydrochloric acid = Potassic chloride + Chromic chloride + Water + Chlorine.

$$\left[\begin{matrix}\mathbf{Cr}O_2Ko\\ O\\ \mathbf{Cr}O_2Ko\end{matrix} + 14HCl = 2KCl + \begin{matrix}\mathbf{Cr}Cl_3\\ \mathbf{Cr}Cl_3\end{matrix} + 7\mathbf{O}H_2 + 3Cl_2.\right]$$

(5.) By the electrolysis of hydrochloric acid.

$$2HCl = \underset{-}{H_2} + \underset{+}{Cl_2}.$$

(6.) By fusing together ammonic nitrate and ammonic chloride. (Maumené.)

$4NH_4NO_3 + 2NH_4Cl = 12H_2O + 5N_2 + Cl_2$.
Ammonic nitrate + Ammonic chloride = Water + Nitrogen + Chlorine.

$[4\mathbf{N}^{v}O_2(N^{v}H_4O) + 2\mathbf{N}H_4Cl = 12\mathbf{O}H_2 + 5\mathbf{N}_2 + Cl_2.]$

(7.) By heating certain chlorides, such as the chlorides of platinum, palladium, and gold. Thus—

(α.) $PtCl_4 = PtCl_2 + Cl_2$. (β.) $PtCl_2 = Pt + Cl_2$.

(8.) By heating a mixture of magnesic chloride and manganic peroxide. (Binks and Macqueen.)

$2MgCl_2 + MnO_2 = 2MgO + MnCl_2 + Cl_2$.
Magnesic chloride + Manganic peroxide = Magnesic oxide + Manganous chloride + Chlorine.

$[2\mathbf{Mg}Cl_2 + \mathbf{Mn}O_2 = 2\mathbf{Mg}O + \mathbf{Mn}Cl_2 + Cl_2.]$

Properties.—(α.) *Sensible.*—Chlorine is a yellowish-green gas, having an insupportable odor.

(β.) *Physiological.*—It is poisonous and intensely irritating, even when largely diluted with air. A bird dies in an atmosphere containing 5 per cent. It rapidly disorganizes all tissues.

(γ.) *Physical.*—It has an experimental specific gravity of 2·45, and a theoretical specific gravity of 2·46. 100 cubic inches, at standard temperature, weigh 76·3 grains, and 1 litre 3·1808 grms. It is one of the heaviest bodies known, gaseous at ordinary temperature.

A pressure of 4 atmospheres (=60 lbs. on square inch) converts it

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into a yellowish green liquid, which has a specific gravity of 1·33. It has never been solidified, but remains liquid at a cold of —220° F. (—140° C.). Liquid chlorine may be prepared either by heating crystals of the hydrate ($Cl_2,10H_2O$), or of platinic chloride ($PtCl_4$) placed in one end of a sealed tube, whilst the other end is immersed in ice and salt.

If the spectrum be passed through chlorine, it will be found that the blue end is cut off and Fraunhofer's lines disturbed. Chlorine does not conduct electricity; it is an electro-negative body, and passes to the + pole of the battery after oxygen and fluorine.

Solubility in water.—The solubility of chlorine in water is as follows:—

At 50° F. (10° C.) water absorbs 2·585 times its bulk of the gas.
At 59° F. (15° C.) ,, ,, 2·368 ,, ,,
At 104° F. (40° C.) ,, ,, 1·365 ,, ,,
(Schönfeld.)

(δ.) *Chemical.*—Chlorine combines with every elementary body. The moist, but not the dry, gas bleaches litmus and turmeric. It is neither combustible, nor a supporter of combustion, but when largely diluted with air, it supports the combustion of a vigorously-burning taper, the chlorine combining with the hydrogen of the hydro-carbon, and setting free the carbon.

Action on the non-metals.—Phosphorus catches fire in chlorine spontaneously, forming PCl_3. Sulphur burns in it feebly. Selenium, boron, and silicon combine with it when heated. It does not combine *directly* either with carbon or with oxygen.

Combinations with hydrogen. — Chlorine has a very strong affinity for hydrogen. Its oxidizing property depends upon this affinity for the hydrogen of water, oxygen being thereby liberated. A mixture of equal volumes of hydrogen and chlorine, combine *with explosion* either by a spark, or when exposed to direct sunlight or to any other light, such as the electric or magnesium lights, containing a good supply of actinic rays; whilst the gases unite *quietly* when exposed to the light of a gas-flame or of diffused daylight, hydrochloric acid in each case being formed.

Action on hydrogenous compounds. — The following reactions of chlorine on compounds of hydrogen should be noted:—

(1.) A taper burns in dilute chlorine with a smoky flame, the chlorine combining with the hydrogen and liberating the carbon. If a jet of chlorine be allowed to play on the flame of a spirit lamp, it becomes luminous, from the solid carbon particles being set free. (2.) Turpentine vapor ($C_{10}H_{16}$) catches fire in chlorine, carbon in large quantity being disengaged ($C_{10}H_{16}+8Cl_2=16HCl+C_{10}$). (3.) If a mixture of chlorine and olefiant gas (C_2H_4) be fired, carbon is set free ($C_2H_4+Cl_4=4HCl+C_2$). (4.) A mixture of chlorine and marsh gas (CH_4) under the influence of sun-light forms chloroform ($CHCl_3$)

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and tetrachloride of carbon (CCl_4). (5.) Ammonia solution is decomposed by chlorine, nitrogen being liberated—

$$8NH_3 + 3Cl_2 = 6(NH_4Cl) + N_2.$$

By its action on a solution of ammonic chloride, chlorine forms the highly explosive body, chloride of nitrogen. (6.) *Water* is decomposed by chlorine. Berthollet originally supposed chlorine to be a compound of oxygen and hydrochloric acid, his experiments being conducted on *moist* chlorine, whereas it was proved by Davy, that the chlorine decomposed the water, fixing the hydrogen (as HCl) and setting free the oxygen. Thus, oxygen may be obtained by passing steam and chlorine through a red-hot tube (see page 57 F.).

Action on organic bodies.—The enormous affinity of chlorine for hydrogen renders its action on organic bodies very powerful. These actions may be thus classified—

(1.) *The chlorine may be simply added to the hydrogen compound.* Thus—

C_2H_4 (*ethene or olefiant gas*) $+ Cl_2 = C_2H_4Cl_2$ (*ethene chloride*).

(2.) *A portion of the hydrogen may be displaced, but without the substitution of chlorine for it.* Thus—

C_2H_6O (*alcohol*) $+ Cl_2 = C_2H_4O$ (*aldehyd*) $+ 2HCl$.

(3.) *A part or all the hydrogens of a compound may be displaced, chlorine being substituted for them.*—This is seen in the following cases—

(*a.*) *The action of chlorine on marsh gas* (CH_4).

$CH_4 + Cl = CH_3Cl$ (*methyl-chloride*) $+ HCl$.
$CH_4 + Cl_2 = CH_2Cl_2$ (*formyl-bichloride*) $+ 2HCl$.
$CH_4 + Cl_3 = CHCl_3$ (*chloroform*) $+ 3HCl$.
$CH_4 + Cl_4 = CCl_4$ (*tetrachloride of carbon*) $+ 4HCl$.

(*β.*) *The action of chlorine on acetic acid* ($C_2H_4O_2$).

$C_2H_4O_2 + Cl = C_2H_3ClO_2$ (*monochloracetic acid*) $+ HCl$.
$C_2H_4O_2 + Cl_2 = C_2H_2Cl_2O_2$ (*dichloracetic acid*) $+ 2HCl$.
$C_2H_4O_2 + Cl_3 = C_2HCl_3O_2$ (*trichloracetic acid*) $+ 3HCl$.

(4.) *This substitution may be only partial.*—Thus, in the action of chlorine on alcohol, 5 hydrogens are replaced by 3 chlorines.

$$\underset{\text{Alcohol.}}{C_2H_6O} + 8Cl = C_2Cl_3HO + 5HCl.$$

It will be noted that this affinity of chlorine for hydrogen on the one hand, and the universal presence of moisture in bodies on the other, renders chlorine indirectly a very powerful oxidizing agent. Thus—

$$2H_2O + 2Cl_2 = 4HCl + O_2.$$

We may here note some of the results of this oxidizing action of chlorine.

(1.) *Various chemical combinations may be effected thereby,* as in the formation of acetic acid from aldehyd.

C_2H_4O (*aldehyd*) $+ H_2O + Cl_2 = C_2H_4O_2$ (*acetic acid*) $+ 2HCl$.

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(2.) Its *bleaching power*, depends on the action of the nascent oxygen set free, by the chlorine combining with the hydrogen of the water. Absolutely dry chlorine has no bleaching action, but in the presence of moisture every organic coloring matter, except carbon, is bleached by it. Mineral colors are not generally acted upon. In the case of indigo, which chlorine bleaches rapidly, it changes it first into isatin, and afterwards into the yellow-tinted chlor-isatine. The following equations represent this action—

(α.) C_8H_5NO (*indigo*) $+ H_2O + Cl_2 = C_8H_5NO_2$(*isatine*) $+ 2HCl$.

(β.) $C_8H_5NO_2$(*isatine*) $+ Cl_2 = C_8H_4ClNO_2$(*chlor-isatine*) $+ HCl$.

Further, a coloring matter bleached by chlorine is destroyed, and cannot, as in bleaching by sulphurous acid, be restored by the action of other re-agents.

(3.) Its *power of disinfection*, again, is an oxidizing action, and depends upon its power of breaking up ammonia and sulphuretted hydrogen, as well as organic matters generally.

Thus it would appear that the chemical activity of chlorine, depends on its affinity for hydrogen, and its power of oxidation, the result of that affinity.

Action on the metals and metallic oxides, etc.—(α.) Its action on the metals is energetic. Powdered antimony, arsenicum, finely divided iron, and Dutch leaf (copper and zinc), light spontaneously when dropped into chlorine. Sodium and magnesium burn in it, forming NaCl and $MgCl_2$. Gold (as leaf gold) combines slowly with it, forming $AuCl_3$.

(β.) Metallic oxides, where the affinity between the oxygen and the metal is feeble, are easily decomposed by chlorine. Thus—

$H_2O + 3HgO$ (*mercuric oxide*) $+ 2Cl_2 = 2HgO,HgCl_2$ (*mercuric oxychloride*) $+ 2HClO$.

(γ.) Chlorine is absorbed by a solution of caustic potash, potassic chloride and potassic hypochlorite being formed.

$$Cl_2 + 2KHO = KCl + KClO + H_2O.$$

If an aqueous solution of chlorine be cooled to 32° F. (0° C.), a solid crystalline hydrate ($Cl_2 10H_2O$) is formed. This hydrate may be seen when chlorine is collected by displacement over very cold water on a cold day. The gas is thus rendered foggy, but clears rapidly on the application of a moderate warmth.

Tests.—Its odor, color, and bleaching properties constitute the chief tests for chlorine in an uncombined state. When free, or combined with a metal, it may be known as follows:—

(1.) *Mercurous nitrate* gives a white precipitate (mercurous chloride or calomel), which is insoluble in nitric acid, and is turned black by ammonia.

(2.) *Argentic nitrate* gives a white curdy precipitate (AgCl), soluble in ammonia, and insoluble in nitric acid. *Free* chlorine produces, with

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an argentic nitrate solution, a trace of argentic chlor*ate* as well as argentic chlor*ide*.

$$6AgNO_3 + 3Cl_2 + 3H_2O = 5AgCl + AgClO_3 + 6HNO_3.$$

Fallacies.—Bromides, iodides, and cyanides. (1.) The *bromide* of silver is of a reddish color. (2.) An *iodide* is known by its reaction on starch paste, when the iodine is set free by the addition of a trace of chlorine water, or else by the reaction of the iodide on palladic nitrate. (3.) A *cyanide* is known by the formation of prussian blue, when acted on by a mixed per- and protosalt of iron.

Estimation.—Chlorine is determined quantitatively as argentic chloride, every 100 parts of which contain 24·74 parts of chlorine.

Uses.—(*a.*) In *nature*, none.

(*b.*) In *the arts*, chlorine is largely used as *a bleaching agent* for linen and cotton cloth. Wool or silk cannot be bleached with chlorine, on account of its injurious action on the fabrics, hence in these cases sulphurous acid is employed. The use of chlorine as applicable to the arts was first suggested by Berthollet, in 1785. Chloride of lime, as it is called, is the form in which it is ordinarily employed. Any acid will liberate the chlorine from this compound.

(*c.*) In *medicine*, the dilute gas is used as an inhalation (vapor chlori, B.P.), *i.e.* moist chlorinated lime from which the carbonic acid of the air sets free a little chlorine. The solution of chlorine (liquor chlori, B.P.), rapidly decomposes, and should be preserved in dark blue bottles. When freshly prepared, it contains more than twice (2·3) its bulk of chlorine, and about 0·75 per cent. by weight.

(*d.*) As a *disinfectant* its action is very intense, owing to its power of breaking up offensive effluvia. If chloride of lime be used for the sick room, a quarter of a pound should be dissolved in about a gallon of water; a piece of flannel dipped in the *clear* liquor should then be freely exposed to the air of the room, from which, by the action of atmospheric carbonic acid, a small but regular evolution of chlorine will take place. For active disinfection, some hydrochloric acid and peroxide of manganese should be mixed on a plate, and placed on a hot brick; the room must then be closed, and left for some hours. Everything metallic should be previously removed from the room.

(*e.*) In its *chemical reactions* chlorine acts in the presence of water as a powerful oxidizer, protoxides being by its action converted into peroxides, sulphur into sulphuric acid, etc.

Compounds of Chlorine and Oxygen.

Chlorine and oxygen are both strongly electro-negative, and have great affinity for hydrogen. Hence their affinity for each other is but slight. The compounds when formed are unstable, and their direct union has not been effected. Possibly there are seven oxides of chlorine, as follows:—

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	The Anhydride	+ H_2O forms the	Acid.	Constitutional formula for the Acids.
1.	Cl_2O or OCl_2.	Hypochlorous.	$2HClO$.	OClH or ClHo.
2.	Cl_2O_2 (?).	(?).	(?).	
3.	Cl_2O_3 or $\begin{cases} OCl. \\ O. \\ OCl. \end{cases}$	Chlorous.	$2HClO_2$.	$\begin{cases} OCl \\ OH \end{cases}$ or OClHo.
4.	Cl_2O_4 or $\begin{cases} OCl. \\ O. \\ O. \\ OCl. \end{cases}$	Chloric peroxide.		
5.	Cl_2O_5 (?).	Chloric.	$2HClO_3$.	$\begin{cases} OCl \\ O \\ OH \end{cases}$ or $\begin{cases} OCl. \\ OHo. \end{cases}$
6.	Cl_2O_6 (?).	(?).	(?).	
7.	Cl_2O_7 (?).	Perchloric.	$2HClO_4$.	$\begin{cases} OCl \\ O \\ O \\ OH \end{cases}$ or $\begin{cases} OCl. \\ O. \\ OHo. \end{cases}$

Nos. 1, 3 and 4 (viz., Cl_2O, Cl_2O_3 and Cl_2O_4) are the only anhydrides that have been isolated. The others are either non-existent or exist only in combination.

There are four oxygen acids which have been regarded for obvious reasons as a series of oxides of hydrochloric acid.

Hypochlorous Anhydride ($Cl_2O = 87$) (OCl_2.)

Molecular weight, 87. *Molecular volume*, ⌈⋮⌉. *Relative weight* (H = 1), 43·5. *Specific gravity* (*Air* = 1) *theoretic*, 3·01. *Liquid boils at* 68° F. (20° C.). 1 *litre weighs* 43·5 *criths* (0·0896 × 43·5) = 3·8976 *grms., and* 100 *cubic inches* 93·0 *grains.*

Preparation.—1. By passing dry chlorine over dry mercuric oxide contained in a cold tube. (Pelouze.)

$$2HgO + 2Cl_2 = Hg_2Cl_2O + Cl_2O.$$

Mercuric oxide + Chlorine = Mercuric oxychloride + Hypochlorous anhydride.

$$\left[2HgO + 2Cl_2 = \begin{cases} HgCl \\ O \\ HgCl \end{cases} + OCl_2. \right]$$

2. By abstracting the water from hypochlorous acid, with glacial phosphoric acid.

$$2HClO - H_2O = Cl_2O.$$

Hypochlorous acid — Water = Hypochlorous anhydride.

3. It is believed by some to be produced in making the euchlorine of Davy, on adding hydrochloric acid to potassic chlorate, but of this there is much doubt.

Properties.—(*a.*) *Sensible and Physiological.*—A deep yellow gas, deeper in color than chlorine. It has a sweet taste, and is intensely suffocating when breathed.

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(β.) *Physical.*—Its specific gravity is 3·01. Two volumes of chlorine and one volume of oxygen form two volumes of the gas (water type). 100 cubic inches weigh 93 grains, and 1 litre 3·897 grammes. By pressure and by the cold of ice and salt (−4° F. or −20° C.), it may be condensed into a red and explosive liquid, which boils at 68° F. (20° C.) Both light, and a very slight heat, such as the warmth of the hand, decompose it. Water dissolves about 200 times its bulk, forming a yellow solution, which has an acrid taste.

(γ.) *Chemical.*—It bleaches litmus and indigo more powerfully than chlorine. It is decomposed by a spark, or by the action of any substance having an affinity for chlorine or for oxygen.

Hypochlorous Acid, (HClO = 52·5) (OClH or ClHo.)

Synonym.—*Hydric hypochlorite.*

Preparation.—(1.) By the action of water on hypochlorous anhydride.

$$Cl_2O + H_2O = 2HClO.$$

Hypochlorous Anhydride + Water = Hypochlorous acid.

[**O**Cl_2 + **O**H_2 = 2**O**ClH.]

(2.) By passing air, charged with hydrochloric acid gas, through a solution of potassic permanganate, acidulated with sulphuric acid, and heated on a water bath. The product is to be collected by distillation. In this reaction HClO is formed from HCl, by direct oxidation ($2HCl + O_2 = 2HClO$).

(3.) By mixing together mercuric oxide, water, and chlorine, and distilling.

$$3HgO + H_2O + 2Cl_2 = 2HgO, HgCl_2 + 2HClO.$$

Mercuric oxide + Water + Chlorine = Mercuric oxychloride + Hypochlorous acid.

$$[3\mathbf{Hg}O + \mathbf{O}H_2 + 2\mathbf{Cl}_2 = \begin{cases} \mathbf{Hg}Cl \\ O \\ Hg \\ O \\ \mathbf{Hg}Cl \end{cases} + 2ClHo.]$$

(4.) By distilling a hypochlorite with an oxy-acid.

$$CaCl_2O_2 + H_2SO_4 = CaSO_4 + 2HClO.$$

Calcic hypochlorite + Sulphuric acid = Calcic sulphate + Hypchlorous acid.

[Ca(OCl)Cl + $\mathbf{S}O_2Ho_2$ = $\mathbf{S}O_2Cao''$ + 2ClHo.]

Properties.—(α.) *Sensible.*—A yellowish-red, chlorine-smelling liquid, having an acrid but not a sour taste.

(β.) *Physiological.*—It acts as an intense irritant poison, and browns the skin.

(γ.) *Physical.*—It boils at 19° F. (— 7° C.), giving off a heavy yellow vapor. It is decomposed by light, into chlorine and chloric acid.

(δ.) *Chemical.*—The gas given off when the acid is heated, is very unstable and highly explosive. The acid has a powerful bleaching

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action; its intensity in this respect being double that of the chlorine it contains, evolving as it does double the oxygen (which in the nascent state is the true bleaching agent) set free by ordinary chlorine. Thus—

(α.) $Cl_2 + OH_2 = 2HCl + O$ (action of common chlorine).

(β.) $ClHO = HCl + O$ (action of hypochlorous acid).

It is decomposed by carbon, iodine, sulphur, selenium, phosphorus, arsenic, and antimony; carbonic, iodic, sulphuric, selenic, phosphoric, arsenic, and antimonic acids being respectively formed.

If a piece of ammonic chloride be placed in the acid, the oily and highly explosive chloride of nitrogen is formed.

If the acid or any of its salts be heated with hydrochloric acid, both acids are decomposed.

$$HCl + HClO = H_2O + Cl_2.$$

Action on the metals.—This varies in a remarkable manner. *Iron* combines with the oxygen of the acid, and sets free chlorine. *Silver* combines with the chlorine of the acid, and sets free oxygen. *Copper* and *mercury* combine with both the chlorine and the oxygen.

Action on metallic compounds.—Plumbic oxide combines with the oxygen, forming PbO_2, and sets free chlorine. Argentic oxide (Ag_2O) combines with the chlorine, forming Ag_2Cl_2, and sets free oxygen. Argentic chloride, by its presence alone, and without being itself decomposed, sets free both oxygen and chlorine, in a gaseous form, from the acid.

On several organic bodies the acid acts vigorously. Thus, urea is broken up by its action.

$$\underset{\text{Urea.}}{CN_2H_4O} + 3HClO = CO_2 + 3HCl + 2H_2O + N_2.$$

It forms with bases the salts known as hypochlorites, which are of great importance in the arts. "Chloride of lime" is prepared by bringing chlorine into contact with recently-slaked lime, and is either a calcic chloride mixed with calcic hypochlorite—

$$(CaCl_2 + Ca2ClO), \text{ or } (\underbrace{Ca''Cl_2}_{\text{Calcic chloride.}} + \underbrace{Cao''Cl_2}_{\text{Calcic hypochlorite.}}),$$

or, as some think, a calcic oxydichloride, or, as it is called, a calcic-chloro-hypochlorite ($Ca(OCl)Cl$) or ($CaOCl_2$).

Chlorous Anhydride ($Cl_2O_3 = 119$). $\begin{cases} OCl \\ O \\ OCl. \end{cases}$

Molecular weight, 119. *Molecular volume* (*anomalous*) $\square\square\square$. *Relative weight* (H = 1), 59·5. *Specific gravity, theoretic*, 4·117; *observed*, 4·070. 1 *litre weighs* 39·7 *criths* (0·0896 × 39·7) = 3·5571 *grms., and* 100 *cubic inches* 126·57 *grs.*

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History.—Discovered by Millon (1842).

Preparation.—1. By deoxidizing chloric acid with nitrous anhydride.

$$2HClO_3 + N_2O_3 = Cl_2O_3 + 2HNO_3.$$

Chloric acid + Nitrous anhydride = Chlorous anhydride + Nitric acid.

$$\left[\begin{Bmatrix} \mathbf{O}Cl \\ \mathbf{O}Ho \end{Bmatrix} + \mathbf{N}_2O_3 = \begin{Bmatrix} \mathbf{O}Cl \\ O \\ \mathbf{O}Cl \end{Bmatrix} + \mathbf{N}O_2Ho. \right]$$

2. By heating a mixture of potassic chlorate, arsenious acid, and nitric acid. The *nitrous acid* (formed by the arsenious acid becoming oxidized at the expense of the oxygen of the nitric acid) acting on the *chloric acid* (produced by the action of the nitric acid on the potassic chlorate) deoxidizes it, and becomes again converted into nitric acid.

$$H_3AsO_3 + 2HNO_3 + 2KClO_3 = H_3AsO_4 + 2KNO_3 + H_2O. + Cl_2O_3.$$

Arsenious acid + Nitric acid + Potassic chlorate = Arsenic acid + Potassic nitrate + Water + Chlorous anhydride.

$$\mathbf{As}Ho_3 + \mathbf{N}O_2Ho + 2\begin{Bmatrix} \mathbf{O}Cl \\ \mathbf{O}Ko \end{Bmatrix} = \mathbf{As}OHo_3 + 2\mathbf{N}O_2Ko + \mathbf{O}H_2 + \begin{Bmatrix} \mathbf{O}Cl. \\ O. \\ \mathbf{O}Cl. \end{Bmatrix}$$

(Tartaric acid may be used in the place of arsenious acid, when carbonic acid will be generated.)

Properties.—It is a yellowish green gas, very irritating when breathed, and stains the skin yellow. It may be condensed by an intense cold into a red liquid (Sp. Gr. 1·33), which is very unstable and explosive, and boils at a temperature a little above the melting point of ice. Water dissolves ten times its bulk of the gas, forming chlorous acid.

It is a powerful oxidizing and bleaching agent. A heat of 134° F. (57 C.) decomposes it into its constituent gases. Most of the non-metals decompose it. The metals have but little action upon it, except arsenicum, which decomposes it, and mercury which absorbs it. *The solution* of the gas, however, oxidizes most metals, forming a mixed chlorate and chloride.

Chlorous Acid ($HClO_2 = 68·5$). ($\mathbf{O}ClHo.$)

Preparation.—By acting on chlorous anhydride with water.

$$Cl_2O_3 + H_2O = 2HClO_2.$$

Chlorous anhydride + Water = Chlorous acid.

$$\begin{Bmatrix} \mathbf{O}Cl \\ O \\ \mathbf{O}Cl \end{Bmatrix} + \mathbf{O}H_2 = 2\mathbf{O}ClHo.$$

Properties.—The acid is unstable. It is decomposed even by carbonic anhydride. It is a powerful oxidizing and bleaching agent,

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and acts on all metals, forming chlorates and chlorides. It is precipitated as plumbic or argentic chlorite with plumbic or argentic nitrate. It forms salts called *Chlorites*. They may be known from the hypochlorites, by their bleaching power not being destroyed by the action of nitric acid and arsenious anhydride.

Chloric Peroxide ($Cl_2O_4 = 135$). $\begin{cases} OCl \\ O \\ O \\ OCl. \end{cases}$

Relative weight 33·75. *Specific gravity, theoretic,* 2·335; *observed,* 2·3227. *Boiling Point,* 68° F. (20° C.).

Synonyms.—*Peroxide of Chlorine; Chloric dioxide; Hypochloric acid; Perchloric oxide.*

History.—Discovered by Davy in 1815.

Preparation.—1. By the action of sulphuric acid on potassic chlorate.

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + OH_2 + Cl_2O_4$$

Potassic chlorate + Sulphuric acid = Potassic perchlorate + Hydric potassic sulphate + Water + Chloric peroxide.

$$3\begin{cases} OCl \\ OKo \end{cases} + 2SO_2Ho_2 = \begin{cases} OCl \\ O \\ OKo \end{cases} + 2SO_2HoKo + OH_2 + \begin{cases} OCl \\ O \\ O \\ OCl. \end{cases}$$

2. By heating a mixture of oxalic acid and potassic chlorate to 149° F. (65°C.). (Calvert.)

Properties.—(α.) *Sensible and Physiological.*—A deep yellow green gas, having a strong chlorine odor and a sweet taste. It is excessively irritating.

(β.) *Physical.*—It has a specific gravity of 2·36; 100 cubic inches weigh 73·16 grains. By a slight pressure, or by a cold of —4° F. (—20° C.), the gas condenses into a red explosive liquid. At a heat of 140° F. (60° C.) it explodes, the gases formed occupying a volume one-third greater than the original gas. It may be preserved in the dark, but is decomposed by light. Water dissolves 20 times its bulk of the gas.

(γ.) *Chemical.*—It is a powerful oxidising and bleaching agent. Its action on many bodies, such as mercury, phosphorus, sugar, and turpentine, is energetic. It neither forms an acid nor salts. It is absorbed, however, by alkaline solutions, a chlorite and a chlorate being formed. Thus—

$$Cl_2O_4 + 2KHO = KClO_2 + KClO_3 + H_2O.$$

Chloric peroxide + Potassic hydrate = Potassic chlorite + Potassic chlorate + Water.

$$\begin{cases} OCl \\ O \\ O \\ OCl \end{cases} + 2OKH = \begin{cases} OCl \\ OK \end{cases} + \begin{cases} OCl \\ OKo \end{cases} + OH_2.$$

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Chloric Acid ($HClO_3 = 84{\cdot}5$). $\begin{cases} OCl \\ O \\ OH \end{cases}$ or $\begin{cases} OCl \\ OHo. \end{cases}$

Synonyms.—*Oxymuriatic acid, hydric chlorate.*

History.—Discovered by Chenevix (1802). Its properties were studied by Guy Lussac (1814).

Preparation.—(1.) A large excess of chlorine is first passed into a strong solution of potassic hydrate, thus producing a potassic chlorate. This is decomposed, the potassic chloride being previously separated by crystallization with hydrofluosilicic acid.

(α.) $6KHO + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$

Potassic hydrate + Chlorine = Potassic chloride + Potassic chlorate + Water.

$6OKH + 3Cl_2 = 5KCl + KClO_3 + 3OH_2.$

(β.) $2KClO_3 + H_2SiF_6 = 2HClO_3 + K_2SiF_6.$

(It is, perhaps, best to form a baric chlorate, and to decompose this with its equivalent of sulphuric acid. After filtering off the baric sulphate, the acid filtrate must be carefully concentrated by evaporation.

Properties.—(α.) *Sensible and Physiological.*—A syrupy liquid, having a strong chloroid smell, a very acid taste, and a powerful corrosive action on the body.

(β.) *Physical.*—Light decomposes it. It is freely soluble in water. A heat of 100° F. (38° C.) breaks it up into oxygen, chlorine, perchloric acid, and water. Thus—

$3HClO_3 = HClO_4 + H_2O + 2O_2 + Cl_2.$

Chloric acid = Perchloric acid + Water + Oxygen + Chlorine.

(γ.) *Chemical.*—Chloric acid is a powerful acid, and even chars paper. It rapidly oxidizes organic matter, but it does not bleach. It is monobasic, like nitric acid. The anhydride has not been isolated. It forms salts called chlorates, which are largely used both in medicine and in the arts. The acid itself has no uses.

Perchloric Acid ($HClO_4 = 100{\cdot}5$). $\begin{cases} OCl \\ O \\ OHo \end{cases}$ or $\begin{cases} OCl \\ O \\ O \\ OH. \end{cases}$

Molecular weight, 100·5. *Specific gravity*, 1·782.

Synonyms.—*Hydric perchlorate.*

History.—Discovered by Count Stadein (1814).

Preparation.—(1.) By distilling potassic perchlorate, with three times its weight of sulphuric acid.

$2KClO_4 + H_2SO_4 = 2HClO_4 + K_2SO_4.$

Potassic perchlorate + Sulphuric acid = Perchloric acid + Potassic sulphate.

$2\begin{cases} OCl \\ O \\ OKo \end{cases} + SO_2Ho_2 = 2\begin{cases} OCl \\ O \\ OHo \end{cases} + SO_2Ko_2$

The impure acid thus formed is then rectified.

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(2.) By the action of heat on chloric acid (prepared by decomposing baric chlorate with sulphuric acid), whereby perchloric acid, together with chlorine, oxygen and water are formed. (*See* Chloric Acid.)

Properties.—(α.) *Sensible and Physiological.*—A colorless liquid, having a very sour taste, even when very dilute. It produces frightful burns when applied to the skin. It turns yellow by keeping, from the liberation of the oxides of chlorine.

(β.) *Physical.*—Very volatile. It has a specific gravity of 1·782 at 60° F. (15·5° C.). It remains liquid at —31°F. (—35° C.).

(γ.) *Chemical.*—The anhydride is unknown. When very dilute it reddens litmus, but does not bleach vegetable colors. In this diluted form it is the most stable of the chlorine oxides. It dissolves iron and zinc, setting free hydrogen. The pure acid is one of the most powerful oxidising bodies known, an explosion resulting when a single drop is brought into contact with any organic substance. In sealed tubes it undergoes spontaneous decomposition and bursts the tubes. It decomposes when distilled. It forms with water a white, silky, crystalline hydrate ($HClO_4,H_2O$) (Crystals of Serullas). This hydrate is decomposed by a heat of 230° F. (110° C.) into the pure acid ($HClO_4$) which distils over, another hydrate ($HClO_4,2H_2O$), a thick oily liquid remaining in the retort, which is not volatile at a lower temperature than 397° F. (203° C.).

The acid forms salts called perchlorates ($M'ClO_4$).

There are several compound oxides of chlorine, the most important of which is *euchlorine*. This was discovered by Davy, and is prepared by heating together hydrochloric acid and a chlorate. It is probably a mixture of chlorine and chloric peroxide. It is a yellow explosive gas.

BROMINE (Br.).

Atomic weight, 80. *Molecular weight*, 160. *Molecular volume* |_|_|. *Atomicity monad* (') (HBr—KBr—AgBr). *Relative weight* (H=1) 80. *Specific gravity* (*Air*=1) *of vapor, theoretic*, 5·536, *observed*, 5·54. *Specific gravity of liquid* (*Water* =1) *at* 32° F., 3·187. *Fuses at* —4 F. (—20° C.) *Boils at* 145·4° F. (63·0° C.).

Synonyms.—*Muride* (*muria*, brine), Balard; *Bromine* (βρῶμος, fetid), Guy Lussac.

History.—Bromine was discovered by Balard, of Montpellier, in August, 1826, in 'bittern,' the mother liquor of sea water, and was at the time supposed to be a compound of chlorine and iodine. Afterwards Balard, Lœwig, and Serullas together, proved its elementary nature.

Natural History.—It never occurs in nature in a free state. (α.) *In the mineral kingdom* it is invariably found in company with chlorine compounds. Sea water contains 0·9 to 1·25 grains of $MgBr_2$ per

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gallon. The Dead Sea water is specially rich in bromine compounds. So also are the mineral springs of Kreuznach, Kissengen, Kershall, etc. Bromine is also found mineralized with silver, zinc, and cadmium. It is found in most samples of rock-salt, and also in coal. (Bussy.) (β.) *In the vegetable kingdom* it is found more or less in all sea plants; and (γ.) *In the animal kingdom* it is found in sponges, liver of cods, etc.

Preparation.—Bromine is usually obtained from the mother liquor of the springs of Kreuznach, Schönbeck, etc.

(1.) *The old process used in preparing it is as follows* :—

(*a*.) Chlorine is first added to the liquor to set free the bromine

$$2KBr + Cl_2 = 2KCl + Br_2.$$

(*b*.) The solution is then shaken up with ether, and after standing, the ethereal layer containing the bromine is decanted.

(*c*.) Caustic potash is now added, and heat applied, whereby the bromine is converted into potassic bromide and potassic bromate—

$$\underset{\text{Potassic hydrate}}{6KHO} + \underset{\text{Bromine}}{3Br_2} = \underset{\text{Potassic bromide}}{5KBr} + \underset{\text{Potassic bromate}}{KBrO_3} + \underset{\text{Water}}{3H_2O}.$$

$$6\mathbf{O}KH + 3Br_2 = 5KBr + \begin{cases} \mathbf{O}K \\ O \\ \mathbf{O}Br \end{cases} + 3\mathbf{O}H_2$$

(*d*.) The residue is now ignited, in order to convert the potassic bromate into potassic bromide :—

$$(2KBrO_3 = 2KBr + 3O_2).$$

(*e*.) The potassic bromide is now dissolved in water and distilled with manganic peroxide and dilute sulphuric acid, when bromine distils over—

$$\underset{\substack{\text{Potassic}\\\text{bromide}}}{2KBr} + \underset{\text{acid}}{2H_2SO_4} + \underset{\substack{\text{Manganic}\\\text{peroxide}}}{MnO_2} = \underset{\substack{\text{Potassic}\\\text{sulphate}}}{K_2SO_4} + \underset{\substack{\text{Manganous}\\\text{sulphate}}}{MnSO_4} + \underset{\text{Water}}{2H_2O} + \underset{\text{Bromine}}{Br_2}.$$

$$2KBr + 2\mathbf{S}O_2Ho_2 + \mathbf{Mn}O_2 = \mathbf{S}O_2Ko_2 + \mathbf{S}O_2Mno'' + 2\mathbf{O}H_2 + Br_2.$$

(*f*.) The bromine is then re-distilled with calcic chloride in order to free it perfectly from water.

(2.) *The new process* of Desfosses, as modified by Mohr and Lœwig consists in distilling the mother liquor at once with manganic peroxide and dilute sulphuric acid, the distillate being afterwards rectified with calcic chloride.

Properties.—(*a*.) *Sensible and physiological.*—Bromine is a dark red liquid, evolving red fumes at ordinary temperatures. It is the only liquid non-metallic element, mercury being the only liquid metallic element. Its odor is fœtid and irritating, and its taste acrid and caustic. It stains the skin a permanent yellow. It is an active poison.

(β.) *Physical.*—Liquid bromine has a specific gravity of 3·187, and its vapor of 5·54. The vapor is evolved at ordinary temperatures. It boils at 145·4 F. (63° C.), and freezes to a brown crystalline solid at —4 F. (—20° C.). 1 part of bromine is soluble in 34 parts of water, the solution having a specific gravity of 1·024. The solution rapidly

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decomposes under the influence of sunlight into oxygen and hydrobromic acid. It is also soluble in alcohol and ether.

(γ.) *Chemical.*—These are in many respects similar to chlorine. As an oxidizing agent it bleaches litmus and indigo. A taper introduced into the concentrated vapor burns badly and with a smoky flame. Phosphorus and some of the metals take fire when brought into contact with it. Turpentine vapor decolorizes bromine vapor, hydrobromic acid being formed. Here its affinity (like that of chlorine) for hydrogen, and its power of displacing it is to be noted. It rapidly attacks organic matters, staining them a yellow color. It combines with all elementary bodies, forming bromides. It also combines with water, forming a hydrate ($Br_2, 10H_2O$).

Tests.—(α.) *In a free state*—Bromine is set free from its compounds by chlorine. It may be known by its red color, and by forming a yellow compound with starch.

(β.) *In combination.*—(1.) *Plumbic acetate* gives a white precipitate of plumbic bromide ($PbBr_2$). (2.) *Argentic nitrate* gives a yellowish-white precipitate of argentic bromide (AgBr) which is insoluble in dilute nitric acid, and of difficult solubility in dilute ammonia.

Uses.—In *the arts*, bromine is used in photography. In *medicine*, the bromide of ammonium (NH_4Br) (ammonii bromidum, B. P.), the ferrous bromide ($FeBr_2$), the potassic bromide (KBr), as well as a solution of bromine (10 minims in 5 ozs. of water) are officinal.

Bromine is a disinfectant, its power being dependent on its affinity for hydrogen, and its consequent oxidising properties.

Compounds of Bromine and Oxygen.

These are probably analogous to the oxides of chlorine; there should be, therefore, four acids and their anhydrides:—

	Anhydride.		+ H_2O form	Acids.	Constitutional formula of Bromine Acids.
1.	Br_2O	OBr_2	Hypobromous.	$2HBrO$.	OBrH or BrHo.
2.	Br_2O_3	..	Bromous.	$2HBrO_2$	OBr / OH or OBrHo.
3.	Br_2O_5	..	Bromic.	$2HBrO_3$	OBr / O / OH or OBr. / OHo.
4.	Br_2O_7	..	Perbromic.	$2HBrO_4$	OBr / O / O / OH or OBr. / O / OHo.

The first anhydride (Br_2O) is the only one known.

Hypobromous Acid (HBrO) may be formed either by agitating mercuric oxide with bromine water (Balard), or by adding bromine to an argentic nitrate solution (Dancer). It is a yellow liquid, easily decomposed by heat; it bleaches powerfully.

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Bromic Acid ($HBrO_3$).—The anhydride is unknown. It may be prepared like chloric acid; also by passing chlorine through bromine water ($Br_2 + 5Cl_2 + 6H_2O = 2HBrO_3 + 10HCl$). It is decomposed by heat.

Perbromic Acid ($HBrO_4$) may be prepared by adding bromine to a solution of perchloric acid. It is a colorless oily liquid, and the most stable of the oxides of bromine.

Compound of Bromine and Chlorine.

Bromous Chloride ($BrCl_3$?) is prepared by passing chlorine through liquid bromine. It is a reddish, volatile, very unstable, pungent liquid, soluble in water, the solution possessing considerable bleaching power.

IODINE (I = 127).

Atomic weight, 127. *Molecular weight*, 254. *Molecular volume*, |_|_|. *Atomicity monad* (′), (HI); *occasionally triad* (ICl_3). *Relative weight* (H = 1), 127. *Specific gravity of solid iodine*, 4·947; *of vapor, theoretic*, 8·7884; *observed*, 8·716. *Melts at* 225° F. (107° C.), *and boils at* 347° F. (175° C.).

History.—Iodine was discovered by Courtois (1812), a French saltpetre manufacturer, on adding sulphuric acid to the waste liquor of kelp. Courtois gave some of it to Desormes and Clement, who published their researches respecting it (1813). It was further examined by Vauquelin, and also by Davy and Guy-Lussac (1813 and 1814).

Natural History.—It never occurs in nature in a free state. (*α.*) In the *mineral kingdom* iodine is found in *sea water* as calcic iodide, but to a less extent than the bromine compound (1 in 250,000: Sonstadt). It is supposed to be the active principle of many *mineral springs* where it is present in combination with potassium, sodium, and magnesium. The spring at Rey, near Freistadt, contains 0·819 part, and that at Halles 0·426 part of magnesic iodide in 10,000 of water. It is also found in the Bath, the Cheltenham, the Leamington, and the Bonnington springs. It is found mineralised with zinc (Silesian ore), lead, mercury, and silver (Mexican ore). It is found in rock salt, in many limestones and dolomites, in Chili nitre (and hence occasionally constitutes an impurity of nitric acid), and occasionally in coal. (*β.*) In *the vegetable kingdom* it is found in sea-weeds as an alkaline iodide, extracted by them from sea-water.

	Iodine in 100 parts of dried plant.
Laminaria digitata...	0·47
Laminaria saccharina	0·16
Fucus vesiculosus	0·01
Fucus nodosus	0·04

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Scotch and Irish sea-weeds contain more iodine than English sea-weeds. It is said to be present in fresh-water plants that grow in running streams (Chatin). (γ.) In the *animal kingdom*, it is found in marine animals, and notably in sponges, oysters, etc. It is an invariable constituent of cod liver oil (0·04 to 0·32 per cent.).

Preparation.—(1.) *Process of Wollaston, as modified by Whytelaw.*

(*a.*) The sea-weeds found on the Scotch coast (specially the laminaria digitata,) are collected during the summer months, dried by exposure, and then burnt without flame, in order to prevent, as far as possible, any loss of sodic iodide. The ash constitutes what is called "kelp," or "varec." A ton of good kelp made from the laminaria digitata will yield from 10 lbs. to 15 lbs. of iodine.

(*b.*) The kelp is first lixiviated with boiling water, whereby about 50 per cent. of solid matter is dissolved, consisting of sodic carbonate, sulphate, sulphite, and sulphide, besides sodic, potassic and magnesic chlorides and iodides.

(*c.*) The solution is then filtered and evaporated to a smaller bulk, in order to separate the sodic carbonate (Scotch soda). It is afterwards still further evaporated to separate the sodic sulphate and chloride.

(*d.*) The residual liquor (Sp. Gr. 1·33 = *iodine ley*) is now mixed with about one-eighth of its bulk of oil of vitriol, and allowed to stand for 24 hours, whereby carbonic and sulphurous acids, and sulphuretted hydrogen are evolved, and sodic sulphate and much free sulphur separated.

(*e.*) The liquid is then filtered and put into a leaden still (iodine still) with manganic peroxide, and heated at a temperature not exceeding 212° F. (100° C.). In this way the formation of chlorine is prevented, and the iodine is obtained as a sublimate.

$$2NaI + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + I_2.$$

Sodic iodide + Manganic oxide + Sulphuric acid = Sodic sulphate + Manganic sulphate + Water + Iodine.

$$2NaI + \mathbf{Mn}O_2 + 2\mathbf{S}O_2Ho_2 = \mathbf{S}O_2Nao_2 + \mathbf{S}O_2Mno'' + 2\mathbf{O}H_2 + I_2.$$

(*f.*) The iodine is now purified by resublimation. Commercial iodine generally contains more or less chloride, cyanide, and bromide of iodine.

(2.) A second process, occasionally adopted, is throwing down the iodine, with a subsalt of copper, as a diniodide of copper. In practice, cupric and ferrous sulphate are mixed with the iodine ley. The subiodide of copper (CuI) formed is then distilled with manganic peroxide and sulphuric acid, whereby iodine is liberated—

$$'Cu'_2I_2 + 2MnO_2 + 4H_2SO_4 = 2CuSO_4 + 2MnSO_4 + 4H_2O + I_2.$$

(3.) *Emil Bechi's Process* (Prize Essay, Florence, 1849). When the solutions are very poor in iodide, Bechi sets free the iodine with nitro-hydrochloric acid, and then filters the liquid through recently ignited lampblack. The lampblack is then washed with a potash solution,

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and the solution evaporated to dryness, the iodine of the solid residue being afterwards liberated by distillation with manganic peroxide and sulphuric acid.

(4.) The iodine is sometimes thrown down from the solution by first adding a little chlorine or nitro-hydrochloric acid, and afterwards raw starch, which sinks to the bottom, carrying the iodine with it.

(5.) The iodine, after being liberated with chlorine, is sometimes extracted from the aqueous solution by shaking it up with benzol. The benzol solution is then treated with a solution of potash, when potassic iodide and potassic iodate are formed (α), from which the iodine may be precipitated with hydrochloric acid (β).

(α.) $6KHO + 3I_2 = 5KI + KIO_3 + 3H_2O$.

(β.) $5KI + KIO_3 + 6HCl = 6KCl + 3H_2O + 3I_2$.

(6.) *In Stanford's process* for the preparation of iodine, the winter weeds (said to contain the most iodine) are dried under cover, submitted to hydraulic pressure, and heated in iron retorts, the gas set free, being collected and utilised.

Properties.—(α). *Sensible.*—Iodine is a black solid, having considerable metallic lustre, and crystallizing in acute rhombic octahedra. Its odor is peculiar, and its taste acrid. It stains the skin yellow. The vapor is a bright violet.

(β.) *Physiological.*—It is an irritant and caustic poison. The vapor is irritating to the lungs, but when largely diluted with air, it has been found in certain cases to act beneficially (vapor iodi, B. P.).

(γ.) *Physical.*—Solid iodine has a specific gravity of 4·947, and the vapor 8·716. The vapor of iodine is the heaviest vapor known, 100 cubic inches weighing 270·32 grains. Iodine volatilizes both at ordinary and at high temperatures unchanged. It fuses at 225° F. (107° C.). It boils, when perfectly dry, at 347° F. (175° C.), but when distilled with water it volatilizes at 212° F. (100° C.). It is a non-conductor of heat and electricity. Its solution in carbonic disulphide is found to be opaque to light rays, but transparent to heat rays. Iodine is dichroic. If the vapor be freely diluted with air, it transmits the red and blue rays of light, and absorbs the green; but the concentrated vapor absorbs the red rays, the blue only being transmitted. Seven thousand parts of water at 60° F. (15·5° C.), dissolve one part of iodine, forming a pale brown liquid, which, in the presence of oxidizable matter, rapidly decomposes, hydriodic acid being formed. Hot water dissolves a larger quantity. The presence of saline matters, and specially of potassic iodide, greatly facilitates solution. Lugol's solution (liquor iodi, B. P.) consists of 20 grs. of iodine, 30 of potassic iodide, and 1 oz. of water. Iodine is far more soluble in alcohol and ether than in water. If water be added to its solution in ether or in alcohol, some of the iodine will be precipitated. A spirituous solution with potassic iodide, forms the tinctura iodi (B. P.) It is even more soluble in chloroform, in benzol, in carbonic disulphide

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and in carbonic tetrachloride, the solutions in these liquids being black, and depositing iodine on evaporation.

(δ.) *Chemical.*—An aqueous solution of iodine bleaches litmus and indigo slightly. A taper introduced into iodine-vapor is immediately extinguished. Iodine more readily combines with *oxygen* than either chlorine or bromine. It forms iodic acid when boiled with nitric acid, neither chlorine nor bromine being oxidized when similarly treated. Nevertheless, direct union between oxygen and iodine cannot be effected.

Iodine forms one compound with chlorine. Phosphorus takes fire when brought into contact with iodine. It combines with sulphur forming a black crystalline body (S_2I_2), used in medicine. Its action on *hydrogen* is not intense, presenting, in this respect, a marked contrast both to chlorine and to bromine. Although the metals generally are attacked by iodine, nevertheless its action on the metals is weaker than that of either chlorine or bromine. Hence it may be displaced by them. If iodine and iron suspended in water, be heated together, an iodide of iron is formed, a compound used in medicine (ferri iodidum, FeI_2) as a pill (pilula ferri iodidi), and a syrup (syrupus ferri iodidi). Iodine forms no definite hydrate with water.

As regards its action on organic bodies, it will sometimes be found to combine with the organic body, and sometimes to oxidize it by combining with hydrogen. But it never displaces hydrogen directly, although it may at times indirectly.

Tests.—(*a.*) *In a free state only.*—It changes starch a blue color (iodide of starch). [This action of starch on free iodine was discovered by Colin and Gaultier de Claubry. 1 part of iodine in a million parts of water may be detected by this means.] Note in respect of this reaction that—

(1.) Combined iodine is unaffected by starch.

(2.) Iodine when present in combination may be set free by the addition of *a trace* of chlorine water, when the blue iodide of starch is formed ($2KI + Cl_2 = 2KCl + I_2$).

(3.) If too much chlorine be added to the solution, it will bleach the blue iodide of starch, and thus the reaction be obscured ($I_2 + 6H_2O + 5Cl_2 = 2HIO_3 + 10HCl$).

(4.) The color may be partially restored by adding a trace of sulphurous acid to the solution ($2HIO_3 + 4H_2O + 5SO_2 = 5H_2SO_4 + I_2$).

(5.) But if an excess of sulphurous acid be added, the color will again disappear ($I_2 + 2H_2O + SO_2 = 2HI + H_2SO_4$).

(6.) The color of the blue iodide of starch disappears on heating the solution to 177° F. (80° C.), but on cooling, the color is partially restored. If the liquid be *boiled,* the color does not re-appear.

(7.) The blue color is also destroyed by the addition of alkalies.

Iodine turns meconine of a blue color.

(*b.*) *In combination.*—The following salts give precipitates as fol-

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lows: *Plumbic acetate*, a yellow; *argentic nitrate*, a yellowish-white; *mercuric chloride*, a red; *palladic nitrate*, a brown; (1 in 50,000); *a little chlorine water and starch*, a blue color.

Uses.—*In the arts.*—Iodine is used in photography, and also in the laboratory as a test reagent for starch. *In medicine* it is used as a resolvent. Courdet of Geneva first suggested the use of the ashes of sponge as a curative agent. It is employed officinally in various forms and combinations, such as potassic iodide, liquor iodi, unguentum iodi, and tinctura iodi, the iodide of sulphur being also used as an unguent, and the iodide of iron as a pill and syrup. As a disinfectant its action is powerful. (Richardson.)

Compounds of Iodine and Oxygen.

Two compounds of iodine and oxygen at most (viz., I_2O_5 and I_2O_7), and probably only one (viz., I_2O_5) have been prepared. This latter may be formed by the action of heat on iodic acid (HIO_3). This serves to illustrate the greater affinity of oxygen for iodine, than for chlorine or for bromine.

Iodic Acid ($HIO_3 = 176$).

Preparation.—(1.) By the action of chlorine on iodine suspended in water (Liebig)—

$$\underset{\text{Iodine}}{I_2} + \underset{\text{Chlorine}}{5Cl_2} + \underset{\text{Water}}{6H_2O} = \underset{\text{Hydrochloric acid}}{10HCl} + \underset{\text{Iodic acid.}}{2HIO_3}.$$

$$\left[I_2 + 5Cl_2 + 6OH_2 = 10HCl + 2\left\{\begin{matrix}OI\\OHo\end{matrix}\right.\right]$$

(2.) By the action of strong nitric acid on iodine. The solution is afterwards evaporated to dryness.

Properties.—(α.) *Physical.*—A white solid, having a sour taste, crystallizing in hexagonal tables (I_2O_5,H_2O:Aq) which are very soluble in water. Heated to 266° F. (130° C.) it becomes I_2O_5,H_2O, and at 338° F. (170° C.) I_2O_5 is formed. At a temperature of 698° F. (370° C.) it is decomposed.

(β.) *Chemical.*—It first reddens and afterwards bleaches litmus. It slowly oxidizes most bodies. It does not blue starch, until acted on with reducing agents, such as SO_2,H_2S, etc., when it is decomposed, iodine being set free, which will then act on starch to form the blue iodide of starch.

Iodic acid is a monobasic acid, and forms iodates.

Periodic Acid ($HIO_4 = 192$). $\left\{\begin{matrix}OI\\O\\OHo.\end{matrix}\right.$

Preparation.—In the process for the preparation of periodic acid there are several distinct steps to be noted:—

(α.) Chlorine is first passed through a solution of sodic iodate containing free soda. (Liebig.)

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$$2NaIO_3 + 6NaHO + 2Cl_2 = 4NaCl + Na_4I_2O_9 + 3H_2O.$$

Sodic iodate + Sodic oxide + Chlorine = Sodic chloride + Sodic periodate (basic) + Water.

$$\left\{\begin{matrix}\mathbf{O}\mathbf{I}\\ \mathbf{O}\mathrm{Nao}\end{matrix}\right. + 6\mathbf{O}\mathrm{NaH} + 2Cl_2 = 4NaCl + Na_4I_2O_9 + 3\mathbf{O}\mathrm{H}_2.$$

(β.) The insoluble basic sodic periodate formed, is collected and treated with argentic nitrate.

$$Na_4I_2O_9 + 4AgNO_3 = 4NaNO_3 + Ag_4I_2O_9.$$

Sodic periodate (basic) + Argentic nitrate = Sodic nitrate + Argentic periodate (basic).

(γ.) The basic argentic periodate formed, is then dissolved in nitric acid, when a neutral argentic periodate is obtained.

$$Ag_4I_2O_9 + 2HNO_3 = 2AgIO_4 + 2AgNO_3 + H_2O.$$

Argentic periodate (basic) + Nitric acid = Argentic periodate (neutral) + Argentic nitrate + Water.

(δ.) This neutral argentic periodate is now boiled in water, when periodic acid and basic argentic periodate is formed.

$$4AgIO_4 + H_2O = Ag_4I_2O_9 + 2HIO_4$$

Argentic periodate (neutral) + Water = Argentic periodate (basic) + Periodic acid.

Properties.—Periodic acid is a crystalline solid, very soluble in water, and easily decomposed by heat.

Compounds of Iodine and Chlorine.

A *protochloride of Iodine* (ICl) may be obtained either directly or by heating a mixture of iodine and potassic chlorate—

$$(I_2 + 3KClO_3 = KClO_4 + KIO_3 + KCl + O_2 + ICl).$$

It is a dark red, oily liquid, solidifying easily. The solid is very deliquescent, and is easily decomposed by water.

The *terchloride of Iodine* (ICl_3) is prepared by heating I_2O_5 with hydrochloric acid ($I_2O_5 + 10HCl = 2Cl_2 + 5H_2O + 2ICl_3$). It is a solid crystalline body, and melts at 77° F. (25° C.) It has no action on starch. When heated, it gives off chlorine.

The *tetrachloride of Iodine* (ICl_4) is supposed to be formed when the protochloride is decomposed ($8ICl = 2ICl_4 + 3I_2$).

A *pentachloride of Iodine* (ICl_5) is also supposed to exist.

Iodine is believed to combine with bromine, forming IBr and IBr_5.

Generalisation on the Halogens (*that is, bodies forming salts, like common salt*), or Salt Radicals (*so called from their forming salts by direct contact with the Metals*), chiefly with reference to Chlorine, Bromine and Iodine.

(1.) In nature these bodies are never found in a free state. Where one is present, all are usually present; as *e. g.* in sea-water, in mineral springs, in marine plants, and in marine animals, etc.

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(2.) They are all monad elements, one volume of the haloid element combining with one volume of hydrogen, to form two volumes of gaseous hydric acids, as HCl; HBr; HI; HF; all of which acids are closely allied in their properties.

(3.) They all attack organic bodies, replacing and displacing hydrogen.

(4.) They all decompose water, forming compounds with the hydrogen, and setting free ozonic oxygen.

(5.) They all bleach, oxidize, and disinfect, by reason of their action on water.

(6.) They all act energetically on the metals, forming typical salts, which are very comparable as mono-, sesqui-, and per-salts.

(7.) They exhibit a remarkable sequence of properties.

(α.) *Form and color.*
- Chlorine is a yellow gas.
- Bromine is a red liquid, boiling at 145·4° F.
- Iodine is a black solid, boiling at 347° F.

(β.) *Specific gravity.*
- Chlorine, 2·47.
- Bromine, 5·54.
- Iodine, 8·72.

(γ.) *Atomic weights.*
- Chlorine, 35·5.
- Bromine, 80·0.
- Iodine, 127·0.

[NOTE.—The intensity of affinity seems to decrease, as the combining number increases.]

(δ) *Compounds with hydrogen.*
- Compound of H and Cl, very stable.
- ,, H and Br, less stable.
- ,, H and I, less stable than HBr.
- ,, H and F, somewhat unstable.

(ε.) The reactions of the salts of the metals also exhibit a peculiar sequence:—

Fluoride of silver, very soluble in water.
Chloride of silver, insoluble in water, soluble in ammonia.
Bromide of silver, ,, ,, slightly soluble in ammonia.
Iodide of silver, ,, ,, insoluble in ammonia.

(ζ.) *The oxy-compounds.*
- Compounds of O and F, non-existent.
- ,, O and Cl, very unstable.
- ,, O and Br, less unstable.
- ,, O and I, stable.

[NOTE.—The stability of the oxygen compounds is in the inverse order to the stability of the hydrogen compounds.]

(η.) Their nitrogen compounds are all explosive.

(θ.) Chlorine is the most electro-negative of the haloids, and displaces bromine from its compounds; bromine stands next, and displaces iodine; nevertheless, in oxy-compounds, iodine will displace chlorine.

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CHAPTER V.

NITROGEN.

NITROGEN:—Atmospheric Air—Its Constituents—Compounds of Nitrogen and Oxygen—Nitrous oxide—Hyponitrous acid—Nitric oxide—Nitrous anhydride—Nitrous acid—Nitric peroxide—Nitric anhydride—Nitric acid—Compounds of Nitrogen and the Haloids—Compounds of Nitrogen with Oxygen and the Haloids.

Atomic Weight, 14. *Molecular Weight*, 28. *Molecular volume*, $\boxed{\ |\ |\ }$. *Atomicity—Pentad* (ˣ), *Triad* (‴); *Monad* (′)—$N^{v}H_4Cl$; $N^{'''}H_3$; N_2O. *Relative Weight* (H=1) 4. *Specific gravity*, 0·9713. 100 *cubic inches weigh* 30·137 *grains, and* 1 *litre* 1 2561 *grammes.*

Synonyms.—*Azote* (Lavoisier); *Nitrogen* (Chaptal).

History.—It was long ago noticed that a combustible body in burning vitiated the air. The Stahlians believed that this vitiation was due to the "phlogiston" liberated by every substance in the act of burning; hence they termed an air so vitiated "phlogisticated air." Dr. Rutherford (1772) of Edinburgh, struck by the change produced in atmospheric air by respiration, suggested that it was a compound of two gases and not an element, and that in the act of breathing, one of these gases was abstracted. Scheele and Lavoisier (1777) independently, proved that air was a mixture of the newly discovered oxygen with another gas which Lavoisier termed *azote* (α and ζωή). This azote, Chaptal (1789) recognised as a constituent of nitre and of nitric acid, and he therefore named it nitrogen.

Natural History.—(α.) In the *mineral kingdom*, nitrogen is found in a free state in the air (to the extent of about 79 per cent. by volume), and also in gaseous volcanic emanations. It is found in combination with oxygen and bases, in nitres, and also with hydrogen, as ammonia, in air and water. (β.) In the *vegetable kingdom* it is present in small quantities in combination in most products of plant-life, as in albumen, the various alkaloids, etc.; and (γ.) In the *animal kingdom* it is found in all fluids and tissues, and plays an important part in the phenomena of life.

Nitrogen present in various animal substances.

	Per cent. by Weight of Nitrogen.		Per cent. by weight of Nitrogen.
Cartilage	15·0	Gluten..	16·0
Fibrin	15·4	Legumin	16·0 to 18·0
Albumen	15·5	Gelatin	18·3
Casein	15·7		
Urea (CH_4N_2O) ..	46·7	Sarcosin ($C_3H_7NO_2$) ..	15·7
Kreatin ($C_4H_9N_3O_2$) ..	32·1	Leucine ($C_6H_{13}NO_2$) ..	12·2
Kreatinin ($C_4H_7N_3O$) ..	37·1	Tyrosin ($C_9H_{11}NO_3$) ..	7·7

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Preparation.—(1.) *By abstracting oxygen from atmospheric air* by one or other of the following methods :—

(α.) By the active combustion of phosphorus.

(β.) By the slow combustion of phosphorus in moist air.

(γ.) By the action of moist iron or some other metallic filings.

(δ.) By the action of moistened alkaline sulphides.

(ϵ.) By the action of potassic pyrogallate.

(ζ.) By admixture with nitric oxide (N_2O_2) and subsequent washing.

(η.) By passing the air over red hot iron, or copper turnings, or best of all, over finely divided copper reduced by hydrogen from the powdered oxide ($Cu_2 + (4N_2{=}O_2)$ *air* $= 2CuO + 4N_2$).

(2.) *By the decomposition of ammonia or of its salts* by such methods as the following :—

(α.) By passing chlorine through an excess of an ammonia solution—

$$\begin{array}{ccccccc} 8NH_3 & + & 3Cl_2 & = & 6NH_4Cl & + & N_2. \\ \text{Ammonia} & + & \text{Chlorine} & = & \text{Ammonia chloride} & + & \text{Nitrogen.} \\ [8\mathbf{N}H_3 & + & 3Cl_2 & = & 6\mathbf{N}H_4Cl & + & N_2]. \end{array}$$

(β.) By heating ammonic nitrite—

$$\begin{array}{ccccc} NH_4NO_2 & = & 2H_2O & + & N_2. \\ \text{Ammonic nitrite} & = & \text{Water} & + & \text{Nitrogen.} \\ [\mathbf{N}O(NH_4O) & = & 2\mathbf{O}H_2 & + & N_2]. \end{array}$$

(γ.) By heating together ammonic chloride and potassic nitrite—

$$\begin{array}{ccccccc} KNO_2 & + & NH_4Cl & = & KCl & + 2H_2O + & N_2. \\ \text{Potassic nitrite} & + & \text{Ammonic chloride} & = & \text{Potassic chloride} & + \text{Water} + & \text{Nitrogen.} \\ [\mathbf{N}OKo & + & \mathbf{N}H_4Cl & = & KCl & + 2\mathbf{O}H_2 + & N_2]. \end{array}$$

(δ.) By heating together ammonic chloride and ammonic nitrate (Maumené's process for getting chlorine) (see page 72).

The chlorine in this case may be got rid of, by washing the products with an alkali.

(ϵ.) By heating together ammonic chloride and potassic dichromate—

$$\begin{array}{ccccccccc} K_2Cr_2O_7 & + & 2NH_4Cl & = & Cr_2O_3 & + & 4H_2O & + & 2KCl & + & N_2. \\ \text{Potassic dichromate} & + & \text{Ammonic chloride} & = & \text{Chromic oxide} & + & \text{Water} & + & \text{Potassic chloride} & + & \text{Nitrogen.} \end{array}$$

$$\left[\begin{cases} \mathbf{Cr}O_2Ko \\ O \\ \mathbf{Cr}O_2Ko \end{cases} + 2\mathbf{N}H_4Cl = \mathbf{Cr}_2O_3 + 4\mathbf{O}H_2 + 2KCl + N_2\right].$$

Properties.—(α.) *Sensible.*—A colorless gas, without odor or taste.

(β.) *Physiological.*—It is not a poison (for we breathe it freely), but it will not support life. In the air it serves the purpose of a diluent, thereby rendering the oxygen less stimulating.

(γ.) *Physical.*—Its specific gravity is 0·9713. It is therefore a little lighter than air; 100 cubic inches weigh 30·119 grains (by calculation 30·033 grains), and 1 litre 1·2561 grms.—14 grains of nitrogen measure at standard temperature and pressure 46·7 cubic inches.

Nitrogen is a permanent gas; that is, it cannot be liquefied by

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cold or by pressure. It is very slightly soluble in water—100 vols. absorb at 32° F.(0° C.), 2·03 vols.; and at 60° F. (15° C.) 1·48 vols. (Bunsen).

(δ.) *Chemical.*—The chemical properties of nitrogen are remarkable for their negative character. It has no action on litmus or turmeric; it neither burns itself nor allows a taper to burn in it; and it does not whiten lime water. Upon *oxygen* it is without action under ordinary conditions, but if sparks be transmitted through a mixture of oxygen and nitrogen, or if nitrogen mixed with hydrogen or ammonia gas be burnt in an atmosphere of oxygen, nitric acid is formed.

Upon *chlorine and the haloids* it has no action, unless nascent, when explosive compounds result. [*Memo.* Being a permanent gas, and so feebly adapted for combination, many of its compounds are explosive.]

Upon *phosphorus, sulphur, selenium, carbon*, etc., it has no action, except in the case of carbon, with which, at a red heat, in the presence of alkalis and alkaline earths, it forms metallic cyanides (M'CN.)

It is said to combine directly with *boron* and *silicon.*

Upon *hydrogen* it has no action, unless the hydrogen be nascent, when ammonia is formed.

Upon the *metals* it has no action, except in the case of tungsten, titanium, magnesium, and tantalum, all of which burn in it when heated, metallic nitrides being formed.

It has no action on *organic bodies.*

Tests.—In a free state we know it by its negative characters; in combination as nitric acid or as ammonia it may be recognised by the special tests for these bodies.

In *organic compounds* we estimate it quantitatively from the ammonia formed by the combustion of the organic matter with soda-lime. If the nitrogen be present in the body as an oxide, it must then be determined as free nitrogen by processes to be hereafter described. (*See* Organic Analysis).

Uses.—These are confined to Nature as a diluent in air, and as a constituent of tissues.

ATMOSPHERIC AIR.

History.—(a.) *Ancient opinions.*—The air was originally regarded as an element. The ancient chemists made no distinction between the various elastic fluids, calling them all *air*, and this *common air*. In 1640, Van Helmont observed differences in airs, and he adopted the word *gas* or *gaz*, to distinguish them. (Thus gas-pinque, gas-siccum, gas-fatiginosum, gas silvestre — De Flatibus.) In 1650, Macquer popularised the word *gas*, and distinguished a gas from a vapor. In 1660 Boyle suspected a difference in the composition of different gases, from their differences of combustibility, etc.

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(β.) *Modern opinions.*—In 1772, Rutherford discovered nitrogen, and in 1774, Priestley discovered oxygen. In 1777, Lavoisier proved that air consisted of a mixture of these two gases, in the proportion of 1 volume of oxygen and 4 volumes of nitrogen. His experiment in proof consisted in boiling mercury for several days in a given bulk of air, noting the loss, the quantity of the calx of mercury formed, and the quantity of oxygen produced on heating the calx. About the same time Scheele and Priestley independently arrived at similar conclusions, the former absorbing the oxygen with potassic sulphide, and the latter with nitric oxide. More careful experiments were afterwards conducted by Cavendish (1781), Prout, Biot and Arago, Dumas and Bousingault, Regnault and others.

Properties.—(α.) *Physical.*—The *specific gravity* of air is regarded as 1; that is, it is regarded at 0° C. and at 30° Bar. Pr. (766 mm.) as the unit and standard of comparison for gases and vapors.

Weight of the air.

100 cubic inches weigh				(Prout)	31·117 grains.
,,	,,	,,	,,	(Biot and Arago)	31·074 ,,
,,	,,	,,	,,	(Dumas and Bousingault)	31·086 ,,
,,	,,	,,	,,	(Regnault)	30·935 ,,
,,	,,	,,	,,	(Mean of the four observations) ..	31·053 ,,

Taking the mean of these experiments, 1 litre of air weighs at 0° C. and 760 mm., 1·2936 grm., and 1 cubic foot, 536·6 grains. Air is therefore 14·45 times heavier than hydrogen, and 816 times lighter than water.

The *average pressure* of the air on the surface of the earth, and at the level of the ocean is equal to 15 lbs. on the square inch, that is, the air is capable of supporting a column of mercury of 30 inches or 760 mm., or a column of water of 34 feet. As we ascend, the pressure diminishes with the density, it being halved for every 3·4 miles. It follows, therefore, that whatever may be the extent of the air, one-half of the atmosphere must be confined to about 3·5 miles of the earth.

The *average temperature* of the air in England is 60° F. (15·56° C.) But this varies at different heights, the temperature decreasing 1° F. for every 300 feet, or 1° C. for every 550 feet.

The *limit of perpetual snow* in this country is about 6,000 feet, and in the tropics at the equator 15,000 feet.

Air is a *refractor of light*, hence the existence of twilight.

(β.) *Chemical.*—Air is a *mechanical mixture* of nitrogen, oxygen and other gases, as proved by the following circumstances:—

(a.) On mixing oxygen and nitrogen in their proper aerial proportions, neither change of volume, nor heat, nor electricity results.

(b.) The relative amounts of oxygen and nitrogen present in the air are not their combining weights, or any multiple thereof.

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(*g.*) When air is shaken up with fresh boiled water, the gases dissolve in their normal proportions, *i. e.*, as 1 of nitrogen to 1·87 of oxygen; and not in the proportion in which they are contained in air, viz., as 4 of nitrogen to 1 of oxygen.

Composition.

General average Analysis of Air (Miller).

	Oxygen	20·61
	Nitrogen	77·95
	Carbonic anhydride	·04
	Aqueous vapor	1·40
	Nitric acid, Ammonia, Carburetted hydrogen	traces.
and in towns	Sulphuretted hydrogen, Sulphurous anhydride	traces.

Constituents of the Air.

(1.) *Oxygen and Nitrogen.*—The proportion of these gases respectively present in air may be estimated in various ways:—

(A.) *By re-agents which absorb the oxygen at ordinary temperatures and leave the nitrogen, as follows:—*

(α.) By mixing a given bulk of air with a given bulk of nitric oxide (N_2O_2) in a graduated tube standing over water. The oxygen present in the air combines with the nitric oxide (N_2O_2) to form nitric peroxide (N_2O_4), which is dissolved as soon as formed by the water in the tube.

Example.—Suppose that to 5 volumes of air we were to add 5 volumes of N_2O_2, we should find that 3 volumes would be immediately absorbed by the water, leaving only 7 volumes in the tube. Of every 3 volumes of N_2O_4 so absorbed 1 volume we know is oxygen. It follows, therefore, that 1 volume of the 5 volumes of the original air was oxygen.

There are many sources of error in this process. The N_2O_2 may contain N_2O, whilst N_2O_3 may be formed in variable proportion, as well as N_2O_4. This process of analysis therefore, although considerably improved by Falconer, Fontana, Cavendish, Humboldt, Guy Lussac, Thénard, and others, is wanting in accuracy.

(β.) By exposing a given volume of air to the action of an alkaline sulphide. (Scheele; improved by De Marti.)

(γ.) By exposing a given volume of air to the action of moist lead shot. (Saussure.)

(δ.) By exposing a given volume of air to the action of sheet copper and dilute sulphuric acid. (Guy Lussac.)

(ε.) By introducing a piece of phosphorus into a given volume of air standing over water. (Berthollet and Parrot; Achard; Brunner; Reboul, etc.)

(ζ.) By a solution of nitric oxide in ferrous sulphate ($4FeSO_4 + N_2O_2$), a brown liquid being formed which rapidly absorbs oxygen. (Sir H. Davy.)

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(η.) Either by an ammoniacal solution of cuprous sulphate, prepared by passing SO_2 through an ammoniacal solution of $CuSO_4$, and dissolving the precipitate formed in ammonia; or by a solution of cuprous oxide (Cu_2O) in ammonia. (Graham.)

(θ.) By a strong solution of pyrogallic acid ($C_{12}H_6O_6$) in caustic potash (potassic pyrogallate).

(B.) *By agents which absorb the oxygen at high temperatures and leave the nitrogen.*—A given volume of air is first passed (1), over *calcic chloride*, then (2), over *caustic potash*, and finally (3), over *ignited copper* reduced from its oxide, severally contained in glass tubes accurately weighed before the experiment is commenced. The increase in the weight of the *calcic chloride* tube indicates the moisture, of the *caustic potash* tube the *carbonic anhydride*, and of the *copper* tube the *oxygen* severally contained in the volume of air operated upon. The residual gas, which is nitrogen, may be collected in an exhausted and weighed globe, the increase in the weight of which gives the nitrogen. (Dumas and Boussingault.)

(C.) *By exploding the air with hydrogen in an eudiometer.* (Regnault, Bunsen, Frankland, Williamson, Angus Smith, Russell, etc.)—Every 1 volume of oxygen requires 2 volumes of hydrogen to form 2 volumes of water gas (H_2O).

Experiment.—To 100 volumes of air add 50 volumes of hydrogen, and explode. The 150 volumes will shrink (water being condensed) to 87 volumes;

$$150 - 87 = 63 \text{ volumes loss;}$$

Of these 63 volumes of H_2O condensed, one-third is oxygen;

Therefore $\frac{63}{3} = 21$ volumes of oxygen in 100 volumes of air.

[Memo.—We may here note, that conversely the quantity of hydrogen present in a mixed gas may be estimated by exploding the gas with *oxygen* and noting the loss, two-thirds of which is hydrogen.]

This combination of oxygen and hydrogen may be effected slowly by using pellets of spongy platinum.

Results of Analysis.—By experimenting on common air the following results were obtained by Dumas and Boussingault and by Regnault:—

		Dumas and Boussingault.	Regnault.	Mean.	In round numbers.
By volume	Nitrogen ..	79·19	79·07	79·13	79
	Oxygen ..	20·81	20·93	20·87	21
		100·00	100·00	100·00	100
By weight	Nitrogen ..	76·99	76 87	76·93	77
	Oxygen ..	23·01	23·13	23·07	23
		100·00	100·00	100·00	100

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The proportions of oxygen and nitrogen present in the air, have been found not to vary more than from 20·80 to 20·97 per cent. by volume. This uniformity is dependent on the operation of winds and upon diffusion, by which gases mix in opposition to gravitation, and when mixed remain so.

The chief differences in the percentage volume of oxygen that have been observed are as follows:—

		Vol. of oxygen per cent.
By *Bunsen* at Marburg	Maximum	20·973
	Minimum	20·840
By *Frankland*	Chamounix (3,000 feet)	20·894
	Grand Mulets (11,000 feet)	20·802
	Top of Mont Blanc (15,732 feet) ...	20·963
By *Miller*	Taken in a balloon at 18,000 feet ...	20·880

(2.) *Ozone.*—The presence of ozone in the air may be detected by test papers. (See page 62.) The general facts relating to ozone may be stated as follows:—

1. More ozone is present during the night than during the day, and most of all is found at day-break.
2. More is found in winter than in summer, and least in autumn.
3. More is found at high than at low levels.
4. More is found on the sea coast, and specially when the wind is blowing from the sea, than inland.
5. More is found in the country than in towns.
6. More is found after a thunderstorm than at any other time; least of all is found on damp foggy days.
7. More is found with western than with eastern winds.
8. The maximum quantity of ozone in the air, never exceeds $\frac{1}{100000}$ part its bulk (Houzeau). Its chief source is atmospheric electricity, and as minor sources the action of aromatic plants and flowers, etc. (See Glaisher's remarks in Appendix to Cholera Reports of Board of Health, 1855, pp. 71—73, 89, 90.)

3. *Aqueous vapor.*—This is determined by instruments called *hygrometers* (ὑγρὸς, moisture, and μέτρον, a measure), hygroscopes, or psychrometers (ψῦχος, cold). A large number of common things such as sea weed, catgut, whipcord, etc., are hygroscopic, and are consequently used as weather instruments.

Daniel's hygrometer, the action of which depends on cooling the air by the evaporation of ether until moisture begins to be deposited, and *Mason's wet and dry bulb thermometers,* are the common instruments in use for measuring the hygroscopicity of the air. The actual amount of moisture in air may be estimated, by passing a given volume of air through a weighed tube containing calcic chloride, its increase of weight after the experiment indicating the amount of moisture present in the volume of air operated upon.

General facts respecting moisture.—(*a.*) Air rarely contains its full

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saturated amount of moisture, except in very cold weather or in very hot tropical seas; in such cases the air is very oppressive.

(*b.*) If the air were saturated with moisture, the amount present would be as follows:—

Amounts of Aqueous Vapour in 1,000 *volumes of Air when saturated.*

Tempt. Fahr. (degrees).	1000 vols. of dry air become when saturated (volumes).	1000 vols. of saturated air contain aq. vap. (volumes).	One cubic foot of air saturated (Ba = 30.)		
			Contains aq. vap. (cubic inches).	Contains aq. vap. (grains).	And it weighs (grains).
10	1002·3	1·12	1·9354	0·84	592·94
20	1003·6	2·29	3·9571	1·30	580·26
30	1005·6	5·57	9·6250	1·97	567·99
40	1008·3	8·23	14·2214	2·86	556·03
50	1012·0	11·76	20·3213	4·10	544·36
60	1017·3	17·06	29·4797	5·77	532·84
70	1024·4	23·82	41·1610	8·01	521·41
80	1034·1	32·98	56·9890	10·98	509·97
90	1047·0	43·93	75·9110	14·85	498·43
100	1063·9	60·07	103·8010	19·84	486·65

(*c.*) The most comfortable degree of saturation is from 66 to 70 per cent. More than this checks evaporation from the body, whilst less causes too great evaporation, thereby parching the mouth and drying the skin.

(*d.*) It has been noted that in certain places, remarkable as health resorts, the degree of saturation is singularly uniform.

(4.) *Carbonic acid.*—This is always present in air. It may be estimated in different ways:—

(*a.*) By passing a given volume of air through a carefully-balanced tube containing caustic potash. The aqueous vapor must first be got rid of by passing the air over chloride of calcium. The increase in the weight of the tube containing caustic potash, indicates the amount of CO_2 present.

(β.) Shake up a gallon bottle of the air to be examined, with a known quantity of lime water. It is only necessary to determine afterwards how much of the lime water remains unneutralized by a standard solution of oxalic acid. (Pettenkofer.)

(γ.) By noting the degree of turbidity produced when a given volume of air is passed through a given bulk either of lime water or of baryta water.

(δ.) By shaking up half an ounce of baryta water (consisting of one half of a cold saturated solution and one-half water) with different bulks of the air under examination. The least turbidity indicates—

With 23	ozs. of air	..	..	..	0·04 CO_2 per cent.
9	,,	..	..	..	0·10 ,,
5	,,	..	..	..	0·20 ,,
$3\frac{1}{2}$	,,	..	..	..	0·30 ,,
$2\frac{3}{4}$	,,	..	..	..	0·40 ,,
2	,,	..	..	..	0·60 ,,
$1\frac{1}{2}$	,,	..	..	..	0·90 ,,

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General facts relating to carbonic acid in the air.—(*a.*) A normal atmosphere contains 4·5 volumes of CO_2 in 10,000 of air (*i.e.*, 0·04 to 0·05 per cent.).

(*b.*) The proportion of carbonic acid is greater at high than at low altitudes. (Frankland).

Chamounix ...	3,000 feet,	6·3 parts of CO_2 per 10,000.	
Grand Mulets ...	11,000 ,,	11·1	,,
Mont Blanc ...	15,732 ,,	6·1	,,

(*c.*) The proportion is slightly greater on the surface of the ocean by day than inland (from the action of the sun on the water?). Lewy found 4·7 parts per 10,000 in the air at the middle of the Atlantic.

(*d.*) The proportion of carbonic anhydride present in the air varies greatly.

Proportions of carbonic acid in the air per 10,000 *parts.*

	Average parts per 10,000.
In cities and towns :—	
London (2·8—4·3)	3·4
Manchester (4·9—15)	5·4
Munich	5·0
Madrid (3·0—8·0)	5·2
Paris (3·6—5·1)	4·9
In dwelling-houses :—	
By day (large rooms) (5·4—8·7)	6·8
,, (small rooms)	12·7
By night (common rooms)	13·4
,, (bed rooms) (28—50)	36·0
In schools :—	
By day, English (9·7—31)	21·5
,, French (27—47)	24·7
,, German	39·2
In mills and workshops (28—30)	29·1
Places of public resort :—	
London law courts (4·8—19·8)	12·3
London theatres (7·6—32·0)	14·9
Manchester theatres (10·2—27·3)	14·8
Paris theatres (23—43)	33·0

(*e.*) Expired air contains from 350 to 500 parts per 10,000, or an average of 425 parts in 10,000 of air.

(*f.*) Roscoe states that the air in rooms never contains more than 0·5 per cent., or 50 parts in 10,000, owing to diffusion and to the porous nature of the walls.

(*g.*) When a chafing dish was lighted and left to burn until the carbonic acid had been generated in sufficient quantity to extinguish the fire, the proportion of CO_2 was found to be 14 per cent. or 1,400 parts per 10,000 of air.

(*h.*) Here it will be well to note the vitiating effects on air of different kinds of fuel and illuminating agents.

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Carbonic acid produced, and air vitiated per hour.

	Carbonic acid produced (cubic inches).	Air vitiated and used (cubic feet).
A man	1,201	723
A horse or cow	14,750	8,591
Batswing burner (3 feet per hour cannel gas) ..	4,304	2,513
Fishtail or Agrand (5 ,, ,, common gas) ..	4,752	2,779
Moderator lamp, consuming 643 grains oil per hour	3,857	2,410
Paraffin ,, ,, 400 ,, ,, ..	2,666	1,658
,, candle ,, 120 ,, ,, ..	800	498
Spermaceti candle ,, 130 ,, ,, ..	809	502
Composite ,, ,, 140 ,, ,, ..	829	515
Wax ,, ,, 168 ,, ,, ..	1,062	670
Tallow ,, ,, 143 ,, ,, ..	858	529

(*i.*) Lastly, we may note that the quantity, according to Pettenkofer, which marks the boundary line between pure and impure air is 0·1 per cent. If, therefore, we find more than 10 parts of CO_2 in 10,000 parts of air, we should be justified in regarding that atmosphere as unwholesome.

(5.) *Ammonia.*—This is generally present in air, although commonly but in small quantities. It was first observed by Liebig. It may be estimated by passing a known volume of air through a known quantity of dilute sulphuric acid, contained in a tube filled with glass beads. The amount of acid left unsaturated must be afterwards determined.

Proportions of ammonia (NH_3) *found in* 1 *million parts of air.*

Fresenius (by day)	0·098
,, (by night)	0·169
Groeger	0·383
Kemp	3·880
Letheby and Tidy	from 4·101 to 6·203

(*Vide* "Quarterly Journal of Agriculture," 1849, p. 160.)

Ammonia is always more abundant in the air in dry than in wet weather, in town than in country, and in summer than in winter.

Proportions of ammonia found in 1 *million parts of rain water.*

	Parts per 1 million.
Boussingault (Liebfrauenberg)	0·80
Lawes and Gilbert (Rothamstead)	1·00
Barral and Boussingault (Paris)	3 to 4
Letheby and Tidy (London Hospital)	4 to 6

(6.) *Nitric acid.*—This is always present in small quantities in the atmosphere, and specially during a thunderstorm, electrical discharges determining the union of the nitrogen and oxygen. Its presence may also be due to the action of ozone on atmospheric ammonia. The acid is present in rain water to the extent, at times, according to Messrs. Lawes and Gilbert, of 3·71 parts in a million.

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Probably ammonia and nitric acid are the source from which plants take their nitrogen, inasmuch as they seem to be unable to assimilate the gas when presented to them in a free state.

(7.) *Sulphurous and sulphuric acids.*—These are always present in the atmosphere of towns where coal is burnt, and may often be seen upon our windows in the form of ammonic sulphate. *Coal* contains from about 0·75 to 4 per cent. of sulphur, the quantity present in common coal being on an average 1·5 per cent. *Coke* contains from 0·6 to 2 per cent. of sulphur, the average quantity being 1·25 per cent. *Coal gas* contains from 12 to 40 grains of sulphur per 100 cubic feet, the average being 20 grains. In certain localities where sulphur is burnt or metals refined, there is often at times a large escape of sulphurous acid into the air. The rain which falls on the roof of the London Hospital College contains from 0·942 grain to 4·357 grains of sulphuric acid (H_2SO_4) per gallon. This is equivalent to from 13·46 to 62·24 parts per million.

(8.) *Organic matters, etc.*—Certain organic vapors, floating particles, germs of fungi, etc., are found in the air, and are revealed by every beam of direct sun-light. That such organic particles are present, the development of mould and of infusoria in organic solutions abundantly testify. Tyndall's researches have shown the power of cotton wool in filtering off these solid particles.

(9.) *Saline matters.*—These are found in the air, and especially in the immediate neighbourhood of the sea.

Compounds of Nitrogen and Oxygen.

These gases have but little tendency to combine directly, nevertheless by indirect combination they form a very complete series of chemical compounds, which may be thus tabulated :—

THE OXIDES OF NITROGEN.

Oxides—formula.	Name.		Acids.	Formula of acids.
N_2O or ON_2	Nitrous oxide	$+H_2O$	=Hyponitrous acid	2HNO or **N**Ho (?)
N_2O_2 or **NO** **NO**	Nitric oxide		No acid	
N_2O_3 or **NO** O **NO**	Nitrous anhydride	$+H_2O$	= Nitrous acid	$2HNO_2$ or **N**OHo
N_2O_4 or NO_2 NO_2	Nitric peroxide	$+H_2O$	= Nitrous acid and Nitric acid	HNO_2 or **N**OHo and HNO_3 or **N**O_2Ho
N_2O_5 or NO_2 O NO_2	Nitric anhydride	$+H_2O$	= Nitric acid	$2HNO_3$ or **N**O_2Ho

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Nitrous Oxide (N_2O=44). (ON_2).

Molecular weight, 44. *Molecular volume*, [|]. *Relative weight* (H=1), 22. *Specific gravity observed*, 1·527. 1 *Litre weighs* (0·0896 × 22) 1·971 *grms., and* 100 *cubic inches* 47·34 *grains.*

Synonyms.—*Dephlogisticated nitrous air* (Priestley); *nitrous oxide* and *laughing gas* (Davy); *protoxide of nitrogen* (most chemists); *nitrogen monoxide.*

History.—Discovered by Priestley (1776) when acting on N_2O_2 with iron filings. Examined by the Dutch chemists (1793) and proved by them to be a compound of nitrogen and oxygen. Its physiological action was investigated by Davy (1809) at the Clifton Pulmonic Institution.

Constitution [N] [N] + [O] = [N₂ O]

14 14 + 16 = $\frac{44}{2}$ or 22.

Preparation.—(1.) By the action of iron filings on nitric oxide (N_2O_2). (Priestley.)

(2.) By heating ammonic nitrate at a temperature of 470° F. (243° C.). (Berthollet and Davy.)

N.B.—If the temperature be above 500° F. (260° C.) other changes occur, nitric oxide and nitrogen being evolved, and a mixture of ammonic nitrite and nitrate subliming. If ammonic chloride be present, the N_2O will be contaminated with chlorine.

NH_4,NO_3 = $2H_2O$ + N_2O

Ammonic nitrate = Water + Nitrous oxide

$[\mathbf{N}O_2(N^vH_4O)$ = $2\mathbf{O}H_2$ + $\mathbf{O}N_2]$

It may also be prepared by heating ammonic chloride with dilute nitric acid (Sp. Gr. 1·2).

(3) By the action of weak nitric acid (Sp. Gr. 1·2) on granulated zinc. (Grotthus.)

$10HNO_3$ + Zn_4 = $4(Zn2NO_3)$ + $5H_2O$ + N_2O

Nitric acid + Zinc = Zincic nitrate + Water + Nitrous oxide

$$\left[10\mathbf{N}O_2Ho + Zn_4 = 4\begin{cases}\mathbf{N}O_2\\ Zno''\\ \mathbf{N}O_2\end{cases} + 5\mathbf{O}H_2 + \mathbf{O}N_2.\right]$$

(4.) By decomposing nitric acid with a hydrochloric acid solution of stannous chloride.

(5.) By passing nitric oxide (N_2O_2) through a solution of sulphurous anhydride.

When the gas is required for inhalation it should be purified by passing it first through a potash solution to get rid of acid vapours, and then through a ferrous sulphate solution to get rid of nitric oxide.

Properties.—(*a.*) *Sensible.*—A sweet-tasted gas, without color or odor.

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(β.) *Physiological.*—When breathed it induces transient intoxication, with strong muscular exertions and uncontrollable laughter (laughing gas). If the inhalation be continued it produces complete anæsthesia, brief as to time, and harmless as to after effects. The liquid and solid nitrous oxide blister the skin when brought into contact with it. (Davy, Roget, Southey, Kingslake, Wedgewood, etc.).

(γ.) *Physical.*—It has a specific gravity of 1·527 (calculated 1·522) —100 cubic inches weigh 47·34 grains (or as calculated 47·18 grains), and 1 litre 1·971 grms. At a temperature of 45° F. (7° C.), and under a pressure of 50 atmospheres (800lbs.), it becomes a colorless liquid, having a specific gravity of 0·908, and boiling at —126° F. (—88° C.). It has the smallest refracting power of any known liquid (Faraday). When the liquid is exposed to the air its evaporation is so rapid that it freezes itself, becoming a white flaky solid which melts at—148° F. (—100° C.). If liquid nitrous oxide be dissolved in carbonic disulphide and evaporated "in vacuo," the lowest known temperature is produced (—220° F.) It is decomposed when heated in a porcelain tube or when exposed to the action of electric sparks.

The gas is freely soluble in water;—100 volumes at 32° F. (0°C.) absorb 30 volumes of the gas; at 60° F. (15·5° C.) it absorbs 78 volumes, and at 75° F. (24° C.) 60 volumes. It is more soluble even in alcohol, in ether, and in the volatile oils, than in water.

(δ.) *Chemical.*— Nitrous oxide is a neutral body without action on litmus or turmeric. It is not combustible, but supports combustion. A taper, phosphorus, charcoal, and sulphur burn in it as vividly as they do in oxygen. It is essential, however, that the combustible body should be burning freely when introduced, as otherwise the temperature will be insufficient to decompose the gas, this being a necessary condition to render it a supporter of combustion.

Nitrous oxide may be known from oxygen as follows:—

(1.) It does not form red fumes with nitric oxide.

(2.) It is very much more soluble in water.

(3.) It is not absorbed by potassic pyrogallate.

(4.) When phosphorus is burnt in it, the residual gas (nitrogen) is identical in volume with that of the original gas, for—

$$\boxed{N|N} + \boxed{O} = \boxed{N_2O}$$

whereas this is not the case when phosphorus is burnt in oxygen.

With hydrogen, nitrous oxide explodes volume for volume—

$$\boxed{N_2 \vdots O} + \boxed{H \vdots H} = \boxed{H_2 \vdots O} + \boxed{N \vdots N}$$

In this manner the composition of the gas may be proved and its quantity in mixture estimated.

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On the metals nitrous oxide has no action in the cold, but the alkaline metals, as well as zinc and iron, when heated burn in it freely. If potassium be burnt in the gas the metal becomes oxidized, and it will be noted that the bulk of nitrogen that remains when the combustion is complete, will be equal to the bulk of the gas originally employed.

Uses.—In *medicine* it is used as an anæsthetic. It is most important that the gas for this purpose should be pure and well washed in potassic and ferrous sulphate solutions.

In *the laboratory* the intense cold produced by the action of carbonic disulphide on its solid or liquid form is valuable in research.

Hyponitrous Acid ($HNO = 31$). (**N**Ho.)

This acid has never been isolated. If, however, an alkaline nitrate be treated with sodium amalgam, a nitrite is first formed ($NaNO_2$), which is afterwards further reduced to the state of hyponitrite ($NaNO$). On neutralizing the alkaline solution with acetic acid, and adding argentic nitrate, a yellow precipitate of argentic hyponitrite ($AgNO$) is formed. The sodic hyponitrite solution, heated with acetic acid, gives off nitrous oxide. (Divers, P.R S., 1871.)

Nitric Oxide (N_2O_2). ($\mathbf{N}O$ / $\mathbf{N}O$ or $'\mathbf{N}''_2O_2$.)

Molecular weight, 60. *Molecular volume* (*anomalous*) *Relative weight*, (H=1), 15. *Specific gravity*, 1·039. 100 *cubic inches weigh* 32·21 *grs.*, *and* 1 *litre* 1·344 *grms.*

Synonyms.—*Nitrous gas* (Priestley); *Binoxide and Deutoxide of Nitrogen; Nitrogen Dinoxide; Azotyl, Nitrosyl.*

Preparation.—(1.) By the action on copper (with or without heat) of dilute nitric acid (Sp. Gr. 1·2). Other metals may be used instead of copper, such as lead, mercury, silver, bismuth, etc., but in these cases a stronger acid is required.

$$3Cu + 8HNO_3 = 3CuN_2O_6 + 4H_2O + N_2O_2.$$

Copper + Nitric acid = Cupric nitrate + Water + Nitric oxide.

$$\left[3Cu + 8\mathbf{N}O_2Ho = 3\left\{\begin{matrix}\mathbf{N}O_2\\ Cuo''\\ \mathbf{N}O_2\end{matrix}\right. + 4OH_2 + {}'\mathbf{N}''_2O_2\right]$$

(2.) By decomposing nitre with ferrous chloride or with ferrous sulphate in their respective acid solutions.

(*a.*) $6FeCl_2 + 8HCl + 2KNO_3 = 3Fe_2Cl_6 + 4H_2O + 2KCl + N_2O_2$

Ferrous chloride + Hydrochloric acid + Potassic nitrate = Ferric chloride + Water + Potassic chloride + Nitric oxide.

$$\left[6\mathbf{Fe}Cl_2 + 8HCl + 2\mathbf{N}O_2Ko = 3\left\{\begin{matrix}\mathbf{Fe}Cl_3\\ \mathbf{Fe}Cl_3\end{matrix}\right. + 4OH_2 + 2KCl + {}'\mathbf{N}''_2O_2\right]$$

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(β.) $6FeSO_4 + 5H_2SO_4 + 2KNO_3 = 3(Fe_2 3SO_4) + 2HKSO_4 + 4H_2O + N_2O_2$

Ferrous sulphate + Sulphuric acid + Potassic nitrate = Ferric sulphate + Hydric potassic sulphate + Water + Nitric oxide.

$6SO_2Feo'' + 5SO_2Ho_2 + 2NO_2Ko = 3S_3O_6Fe_2^{vi} + 2SO_3HoKo + 4OH_2 + N_2O_2$

(3.) By passing ammonia gas over heated manganic peroxide.

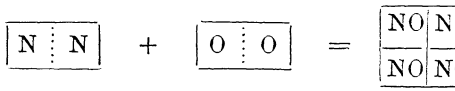
$5MnO_2 + 2NH_3 = 5MnO + 3H_2O + N_2O_2$

Manganic peroxide + Ammonia = Manganous oxide + Water + Nitric oxide.

$[5MnO_2 + 2NH_3 = 5MnO + 3OH_2 + N''_2O_2.]$

Properties.—(α.) *Sensible and physiological.*—A colorless gas having a strong and disagreeable odor. It produces violent irritation when breathed (Davy). It destroys life if respired for more than a few seconds.

(β.) *Physical.*—Nitric oxide consists of equal volumes of nitrogen and oxygen united without condensation. That is, 2 vols. of NO, weighing 30, consist of 1 volume of N=14, and 1 volume of O=16. It follows, therefore, that NO and not N_2O_2 is its true formula.



Its specific gravity, both by experiment and by calculation ($15 \times 0{\cdot}0693$) is 1·039. 100 cubic inches weigh 32·21 grains, and 1 litre 1·344 grms. It cannot be liquefied by cold or by pressure. It is the most stable of all the nitrogen oxides, and is consequently the oxide most commonly formed by the decomposition of the other oxides. For neither a red heat (or, indeed, any heat short of a white heat) nor electric sparks decompose it when the gas is quite dry, although in the presence of moisture both heat and electricity decompose it. 100 volumes of water dissolve 5 volumes of the gas, and 100 volumes of alcohol 27·4 volumes.

(γ.) *Chemical.*—Provided no free oxygen be present, nitric oxide is neutral both to litmus and turmeric. It neither burns nor supports combustion unless the combustible body, when introduced, be burning sufficiently energetically to effect its decomposition. Under such circumstances *carbon* burns in it freely, forming nitrogen and carbonic anhydride; and also *phosphorus*, leaving pure nitrogen.

Its special characteristic is its affinity for oxygen. The red fumes of nitrous anhydride (N_2O_3) and nitric peroxide (N_2O_4), formed by its combination with oxygen, distinguish it from all other gases. The proportions of these two gases formed when nitric oxide is mixed with oxygen vary, and, inasmuch as they have different solubilities, it is not possible to estimate the oxygen accurately in any mixture by this means (see page 97). It has no action on hydrogen at ordinary temperatures. A mixture of equal volumes of hydrogen and of nitric oxide, burns when ignited, with a green flame, but without explosion: whereas a mixture in like proportion of hydrogen and nitrous oxide

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explodes. When, however, a mixture of nitric oxide and hydrogen is passed over heated platinum black, ammonia is formed ($N_2O_2+5H_2=2NH_3+2H_2O$). Mixed with the vapor of carbonic disulphide it burns with an intensely white light.

Potassium and sodium, when heated, burn in the gas. It is also decomposed in the presence of moisture by red-hot iron and tin, the residual gas (nitrogen) constituting in each case one-half of the original gas. Moist iron and moist zinc slowly decompose it, nitrous oxide (N_2O) being formed.

Solutions of *ferrous* and *chromous* salts absorb it freely, forming a dark olive-brown compound, consisting of four parts of a ferrous or chromous salt with two parts of nitrous oxide ($4FeSO_4,N_2O_2$) (Péligot). These solutions absorb oxygen freely, and, when heated, evolve their nitric oxide unchanged.

Other metallic salts (such as stannous and mercurous salts) also absorb the gas, but with mutual decomposition. They cannot therefore, as in the case of ferrous and chromous salts, yield the nitric oxide after absorption in an unchanged state.

The gas is absorbed by nitric acid, a red, green, or blue solution resulting, the color depending on the dilution of the acid. Probably in these cases a higher nitrogen oxide (N_2O_4) is formed.

Nitric oxide has a basylous character, and, like the alkaline metals, is capable of replacing hydrogen in many compounds. Thus, like sodium, it will replace one of the hydrogens of alcohol:—

$C_2H_5(OH)$	—	$C_2H_5(ONa)$	—	$C_2H_5(O(NO))$.
Alcohol	—	Sodic ethylate	—	Nitrous ether.

Nitric oxide forms two chlorides, viz., chloride of azotyl or nitrosyle (NOCl) and bichloride of azotyl ($NOCl_2$). Corresponding to sodic oxide (Na_2O) there is an oxide of nitric oxide, viz., nitrous anhydride [N_2O_3 or $(NO)_2O$]; corresponding to sodic hydrate (NaHO), there is nitrous acid ((NO)HO); and corresponding to hydric-sodic sulphate ($NaHSO_4$) there is $(NO)HSO_4$.

Its only use is in chemistry, as a test for the presence of free oxygen.

Nitrous Anhydride (N_2O_3) $\left\{\begin{matrix}\mathbf{N}'''\mathrm{O}\\ \mathrm{O}\\ \mathbf{N}'''\mathrm{O}\end{matrix}\right.$

Molecular weight (*probable*), 76. *Molecular volume*, (*probable*) □. *Specific gravity* (*theoretic*) 2·63.

Synonyms. *Nitrous acid* (Davy, Graham, Gmelin, Berzelius, Miller); *Pernitrous acid* (Guy Lussac); *Hyponitrous acid* (Turner, Brande, and Liebig); *Nitrous oxide* (Watts); *Nitric trioxide* (Roscoe); *Nitrogen trioxide* (Fownes, Roscoe).

Preparation. (1.) By mixing four volumes of *dry* nitric oxide

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(N_2O_2) with one volume of dry oxygen, and cooling the mixture to 0°F. (—18°C.), ($N_2O_2+O=N_2O_3$).

(2.) By the action of arsenious anhydride upon nitric acid.

$As_2O_3 + 2HNO_3 = As_2O_5 + H_2O + N_2O_3$

Arsenious anhydride + Nitric acid = Arsenic anhydride + Water + Nitrous anhydride.

[$\mathbf{As}_2O_3 + 2\mathbf{N}O_2Ho = \mathbf{As}_2O_5 + \mathbf{O}H_2 + \mathbf{N}_2O_3$]

(3.) By the action of strong nitric acid on silver.

$6HNO_3 + 2Ag_2 = 4AgNO_3 + 3H_2O + N_2O_3$

Nitric acid + Silver = Argentic nitrate + Water + Nitrous anhydride.

[$6\mathbf{N}O_2Ho + 2Ag_2 = 4\mathbf{N}O_2Ago + 3\mathbf{O}H_2 + \mathbf{N}_2O_3$

(4.) By heating together one part of starch and eight parts of nitric acid (1·2 specific gravity).

Properties. (α.) *Sensible and physical.*—A deep red gas, condensing at 0° F. (—17·8 C.) to a blue liquid, which evolves red fumes.

(β.) *Chemical.*—Nitrous anhydride combines with sulphurous anhydride to form white flakes, such as occur in the oil of vitriol leaden chamber ($SO_2+N_2O_3$). The gas is soluble in nitric acid, forming a colored solution. By the action of *a little ice cold water* on the gas, nitrous acid is formed, the liquid becoming blue ($N_2O_3+H_2O=2HNO_2$). This acid is a very unstable body, the *addition of an excess of water even at ordinary temperatures*, decomposing it into nitric acid and nitric oxide ($3N_2O_3+H_2O=2HNO_3+2N_2O_2$).

Nitrous Acid (HNO_2) (**N**OHO).

Molecular weight, 47.

Preparation.—(1.) By mixing a little ice cold water with nitrous anhydride—

$N_2O_3 + H_2O = 2HNO_2$.

Nitrous anhydride + Water = Nitrous acid.

[$\mathbf{N}_2O_3 + \mathbf{O}H_2 = 2\mathbf{N}OHo$.]

(2.) By the oxidation of ammonia; as, *e. g.*, by placing a red-hot platinum wire in a mixture of air and ammonia gas, or by shaking up a few drops of ammonia solution with metallic copper in a bottle containing air. (Schönbein.)

Properties.—Nitrous acid is an ill-defined and unstable compound. It forms salts called nitrites. Of these salts, as of the acid itself, our knowledge is imperfect. Potassic nitrite (KNO_2) is obtained by heating potassic nitrate (KNO_3) so as to drive off some of its oxygen. Nitrous acid imparts the red color to nitric acid, acquired by it on exposure to light. It is decomposed by water into nitric acid and nitric oxide.

The acid, as well as acidulated solutions of the nitrites, acts both as a reducing and as an oxidizing agent; thus—

(α.) As an *oxidizing* agent ($4HNO_2=2N_2O_2+2H_2O+O_2$) it decolorizes indigo, converts ferrous into ferric salts, oxidizes iodides, and liberates iodine from potassic iodide.

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(β.) As a *reducing* agent ($2HNO_2+O_2=2HNO_3$) it acts on permanganates and chromates, and sets free metallic gold and mercury from their combinations.

Nitric Peroxide (N_2O_4 or NO_2) $\left\{\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}\right.$ or $'\mathbf{N}_2^{IV}O_4$.

Molecular weight, 92; *Molecular volume*, $\square$ or $\boxplus$. *Specific gravity at* 309·2 F. (154° C.)=1·58. 1 *litre weighs* (0·0896 × 23)=2·06 *grms.*, *or* (0·0896 × 46)=4·12 *grms.*

Synonyms. *Nitrous acid* (Turner, Brande, etc.); *Hyponitric acid* (Gmelin); *Nitrous gas* (Berzelius); *Peroxide of nitrogen* (Graham, Odling, etc.); *Pernitric oxide*; *Nitrogen tetroxide* (Roscoe); *Nitryl* (because of its basylous action).

History.—First obtained by Davy by mixing nitric oxide with oxygen.

Preparation. (1.) By mixing two parts of nitric oxide with one part of oxygen. The mixture must be passed into dry and ice cold tubes (Péligot).

(2.) By heating very dry plumbic nitrate. (The N_2O_4 in this process is mixed with one-fourth its volume of oxygen).

$2(Pb2NO_3)$	=	$2PbO$	+	$2N_2O_4$	+	O_2.
Plumbic nitrate	=	Plumbic oxide	+	Nitric peroxide	+	Oxygen.

$$\left[\ 2\left\{\begin{matrix}\mathbf{N}O_2\\ Pbo''\\ \mathbf{N}O_2\end{matrix}\right. = 2\mathbf{Pb}O + 2'N_2^{IV}O_4 + O_2\ \right]$$

(3.) By the action of tin on nitric acid.

Sn_5	+	$20HNO_3$	=	$Sn_5O_{10},5H_2O$	+	$5H_2O$	+	$10N_2O_4$.
Tin	+	Nitric acid	=	Metastannic acid	+	Water	+	Nitric peroxide.
$[Sn_5$	+	$20\mathbf{N}O_2Ho$	=	$\mathbf{Sn}_5O_5,Ho_{10}$	+	$5\mathbf{O}H_2$	+	$10'\mathbf{N}_2^{IV}O_4]$

(4.) By the action of nitryl chloride on argentic nitrite.

NO_2Cl	+	$AgNO_2$	=	$AgCl$	+	N_2O_4
Nitryl Chloride	+	Argentic nitrite	=	Argentic chloride	+	Nitric peroxide.
$[\mathbf{N}O_2Cl$	+	$\mathbf{N}OAgo$	=	$AgCl$	+	$'\mathbf{N}_2^{IV}O_4]$

Properties.—(α.) *Sensible and Physiological.*—A brownish, red gas, very irritating when inhaled. It stains the skin a yellow colour.

(β.) *Physical.*—Its relative weight (*i.e.*, its weight compared with hydrogen at the same temperature) diminishes with a rise of temperature. At 275° F. (135° C.) it is 23 times as heavy as hydrogen; therefore the molecule at this temperature is 46 (23 × 2), and is expressed by the formula NO_2; but as the temperature is lowered, its specific gravity increases, and no doubt under such circumstances N_2O_4 (which at higher temperatures is decomposed into $2NO_2$) ex-

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presses its molecular state. Actual experiments give the following results (Deville and Troost) :—

At	80·0° F. (26·7° C.)	Specific Gravity	2·65.
,,	140·3° F. (60·2° C.)	,,	2·08.
,,	177·0° F. (80·6° C.)	,,	1·80.
,,	212·1° F. (100·1° C.)	,,	1·68.
,,	309·2° F. (154·0° C.)	,,	1·58.
,,	361·7° F. (183·2° C.)	,,	1·57.

Thus it would seem that the molecule of nitric peroxide is differently constituted at different temperatures.

Action of heat.—When the gas is perfectly dry, a cold of 0° F. (—17·8° C.) condenses it into colourless, transparent, prismatic crystals. These crystals melt at 14° F. (—10° C.), forming a colourless liquid, which, at 16° F. (—9° C.), becomes yellowish green, and gradually deepens in color as the temperature rises to 71·6° F. (22·6° C.), when the liquid boils. The liquid has a specific gravity of 1·451, and cannot be solidified a second time at a temperature above —22° F. (—30° C.).

By the action of heat on the vapor it becomes gradually darker until at 104° F. (40° C.) it is almost black. It is decomposed by electric sparks, and by a temperature above a red heat. The action of water upon it will be studied under its chemical properties.

(γ.) *Chemical.*—Nitric peroxide reddens litmus. It was long considered an anhydride, but it always forms, when decomposed by bases, a mixture of a nitrite and a nitrate.

It does not support the combustion of bodies unless they be burning energetically when introduced. Chlorine combines with it indirectly but not directly, to form an oily liquid called chloride of nitryl (NO_2Cl).

When a mixture of the gas and hydrogen is passed over spongy platinum, the nitric peroxide is decomposed with elevation of temperature, water and ammonia being formed ($N_2O_4+7H_2=2NH_3+4H_2O$). When a mixture of sulphuretted hydrogen and the gas is similarly treated, water and ammonia are formed, and sulphur is precipitated ($N_2O_4+7H_2S=2NH_3+4H_2O+7S$).

Its *action on water* is remarkable. If a trace of moisture be present when the gas is first prepared and subjected to the freezing mixture, it forms a green liquid, having the probable formula of ($N_2O_3,N_2O_5H_2O$). This liquid turns yellow at 14° F. (—10° C.), and becomes red at ordinary temperatures. It freezes at—40° F. (—40° C.), and boils at 82° F. (28° C.). Like the liquid nitric peroxide, it freely evolves red fumes at ordinary temperatures. But if a very little ice-cold water be added to the liquid nitric peroxide at 0° F. (—17·8 C.), two liquid layers are immediately formed, the *upper layer* being the least coloured, and consisting of nitric acid, and *the lower layer*, the most coloured, consisting of nitrous acid and nitrous anhydride.

$$3N_2O_4 + 2H_2O = 3HNO_3 + HNO_2 + N_2O_3$$

Nitric peroxide + Water = Nitric acid + Nitrous acid + Nitrous anhydride.

$$2\mathbf{N}_2O_4 + \mathbf{O}H_2 = 3\mathbf{N}O_2Ho + \mathbf{N}OHo + \mathbf{N}_2O_3.$$

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If at this low temperature more water be added to the liquid, nothing but nitrous and nitric acids will remain;—

N_2O_4	+	H_2O	=	HNO_3	+	HNO_2
Nitric peroxide	+	Water	=	Nitric acid	+	Nitrous acid.
[$\mathbf{N}_2O_4$	+	$\mathbf{O}H_2$	=	$\mathbf{N}O_2Ho$	+	$\mathbf{N}OHo.$]

If water be added to the liquid peroxide *at ordinary temperatures*, the solution passes through various shades of color, viz., orange, yellow, green, and blue, finally becoming colorless, an escape of nitric oxide taking place all the time.

$3N_2O_4$	+	$2H_2O$	=	$4HNO_3$	+	N_2O_2.
Nitric peroxide	+	Water	=	Nitric acid	+	Nitric oxide.
[$3\mathbf{N}_2O_4$	+	$2\mathbf{O}H_2$	=	$4\mathbf{N}O_2Ho$	+	$N_2O_2.$]

Thus, it would seem that a variety of decompositions may be effected, according to the proportions of water mixed with the nitric peroxide, and the temperature at which the water is added, but that in every case nitric acid is formed. These reactions may be thus tabulated—

Cold 0° F. (−17·4° C.)	$4N_2O_4$	+ H_2O	=	$2HNO_3$ Nitric acid	+	N_2O_5 Nitric anhydride	+	$2N_2O_3$ Nitrous anhydride
	$3N_2O_4$	+ $2H_2O$	=	$3HNO_3$ Nitric acid	+	HNO_2 Nitrous acid	+	N_2O_3 Nitrous anhydride
	$3N_2O_4$	+ $3H_2O$	=	$3HNO_3$ Nitric acid	+	$3HNO_2$ Nitrous acid		
Ordinary temperatures	$3N_2O_4$	+ $2H_2O$	=	$4HNO_3$ Nitric acid	+	N_2O_2 Nitric oxide		

Action of Acids.—Sulphuric acid absorbs the gas, forming with it a crystalline compound ($2H_2SO_4,N_2O_4SO_3$). Nitric acid dissolves it, and forms the deep red, green, and blue liquids, called in commerce "nitric acid fortissimus." The color of these liquids is destroyed by dilution. Hydrochloric acid forms with it several chlorinated compounds.

Action on the Metals and their Compounds.—Most metals are oxidized by it. Potassium takes fire in it spontaneously. Iron decomposes it at a red heat, evolving nitrogen. Potassium, lead, mercury, etc. form a nitrate with the liquid peroxide, nitric oxide being expelled ($2N_2O_4+K_2=2KNO_3+N_2O_2$). With metallic oxides and hydrates a nitrate and a nitrite of the metal are formed;—

N_2O_4	+	$2HKO$	=	KNO_3	+	KNO_2	+ H_2O.
Nitric peroxide	+	Potassic hydrate	=	Potassic nitrate	+	Potassic nitrite	+ Water.
[$\mathbf{N}_2O_4$	+	$2\mathbf{O}KH$	=	$\mathbf{N}O_2Ko$	+	$\mathbf{N}OKo$	+ $\mathbf{O}H_2$.]

Action of Organic Bodies.—In some cases nitric peroxide combines directly with the organic body; thus C_5H_{10}(*Amylene*)$+N_2O_4=C_5H_{10}N_2O_4$. In other cases it replaces hydrogen, forming nitro—compounds which

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are often explosive. They are produced by the direct action of *fuming* nitric acid (mixed with sulphuric acid in order to increase its strength) on the organic body. The following are illustrations:—

		Nitro compounds.	
Benzole C_6H_6	forms	$C_6H_5(NO_2)$	Nitro-benzole.
,,	,,	$C_6H_42(NO_2)$	Dinitro-benzole.
Napthalene $C_{10}H_8$	,,	$C_{10}H_7(NO_2)$	Nitro-napthalene.
Glycerine $C_3H_8O_3$	,,	$C_3H_53(NO_2)O_3$	Nitro-glycerine.
Mannite $C_6H_{14}O_6$	,,	$C_6H_86(NO_2)O_6$	Nitro-mannite.
Cellulose $C_6H_{10}O_5$	,,	$C_6H_82(NO_2)O_5$	Nitro-cellulose.
Starch $C_{12}H_{20}O_{10}$	,,	$C_{12}H_{19}(NO_2)O_{10}$	Xyloidin.

The only use of the nitric peroxide is as an agent in the sulphuric acid manufacture.

General Remarks on the Oxides of Nitrogen.

Before we proceed to examine the next oxide of nitrogen, it is well that we should generalise on the facts relative to the oxides of nitrogen that we have thus far investigated. Note, then—

(1.) That the proportions of oxygen in the series advance in a regularly ascending order—N_2O, N_2O_2, N_2O_3, N_2O_4.

(2.) That the names of the oxides are very confusing.

(3.) That they have all been discovered since the time of Priestley (1776).

(4.) That none of them have been found in nature in a free state, and that only one (viz., N_2O_3 as nitrites) has even been found combined.

(5.) That they may all be prepared by the deoxidation and dehydration of nitric acid, and that two of them (viz., N_2O_3 and N_2O_4) may be prepared by the oxidation of N_2O_2.

This may be shown thus:—

$2\,HNO_3 - H_2O = N_2O_5$ Nitric anhydride.
$2\,HNO_3 - H_2O - O = N_2O_4$ Nitric peroxide.
$2\,HNO_3 - H_2O - O_2 = N_2O_3$ Nitrous anhydride.
$2\,HNO_3 - H_2O - O_3 = N_2O_2$ Nitric oxide.
$2\,HNO_3 - H_2O - O_4 = N_2O$ Nitrous oxide.

We may thus summarize the preparation of the nitrogen oxides:—

(i.) N_2O_5 is prepared by the action of *phosphoric anhydride* on nitric acid.

$$6\,HNO_3 + P_2O_5 = 2H_3PO_4 + 3N_2O_5.$$

(ii.) N_2O_4 is prepared by the action of *tin* on nitric acid.

$$20HNO_3 + Sn_5 = Sn_5O_{10},\ 5H_2O + 5H_2O + 10N_2O_4.$$

(iii.) N_2O_3 is prepared by the action of *silver* on nitric acid.

$$6HNO_3 + 2Ag_2 = 4AgNO_3 + 3H_2O + N_2O_3.$$

(iv.) N_2O_2 is prepared by the action of *copper* on nitric acid (Sp. Gr. 1·25).

$$8HNO_3 + 3Cu = 3CuN_2O_6 + 4H_2O + N_2O_2.$$

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(v.) N_2O is prepared by the action of *zinc* on nitric acid.

$$10HNO_3 + 4Zn = 4ZnN_2O_6 + 5H_2O + N_2O.$$

(6.) That they are all gases, the first two of the series (viz. N_2O and N_2O_2) being colorless, and the last two red. One (viz. N_2O) is respirable, and the others are irrespirable.

(7.) That their specific gravities determine their molecular constitution. The molecular volume of N_2O_2 is anomalous and would be, therefore, more correctly NO; whilst in N_2O_4 the molecule is differently constituted at different temperatures.

(8.) By an intense cold three of them may be liquefied and solidified; viz., N_2O, N_2O_3, and N_2O_4. N_2O_2 is a permanent gas.

(9.) At high temperatures they may all be decomposed, when combustible bodies burn in them.

(10.) *Action of Metals.*—They are all decomposed by the alkaline metals, and also by iron and zinc when heated in contact with them.

(11.) *Action of Water.*—The first two (N_2O and N_2O_2) of the series are soluble in water, whilst the remaining two (viz., N_2O_3 and N_2O_4) are decomposed by it, and are converted into nitric acid and into other oxides, viz., N_2O_4, N_2O_3, N_2O_2, and HNO_2.

(12.) *Action of Acids.*—*Sulphuric acid* is without action upon them. *Sulphuric anhydride* unites with N_2O_3 and N_2O_4 to form the white flakes of the oil of vitriol leaden chamber. *Nitric acid* forms dark colored liquids with N_2O_2, N_2O_3, and N_2O_4.

(13.) Two of them (viz. N_2O_2 and N_2O_4) are *basylous* in character, either (α) combining with chlorine to form chlorides (as *e.g.*, N_2O_2), or (β) displacing hydrogen in organic compounds (as *e.g.*, N_2O_4).

(14.) Nitrous oxide is used as an anæsthetic, but the other members of the series have little use other than the part they play in the manufacture of oil of vitriol.

(15.) They all set iodine free (like ozone) from potassic iodide.

Nitric Anhydride, $N_2O_5=108$ ($\mathbf{N}_2O_5$).

Molecular weight (*probable*), 108. *Molecular volume* (*probable*) .
Melts at 85° F. (29·5° C.) *Boils at* 113° F. (45° C.)

History.—First prepared by Deville in 1848.

Preparation. (1.) By passing very dry chlorine over hot argentic nitrate (Deville).

$4AgNO_3$	+	$2Cl_2$	=	$4AgCl$	+	$2N_2O_5$	+	O_2.
Argentic nitrate	+	Chlorine	=	Argentic chloride	+	Nitric anhydride	+	Oxygen.
[$4\mathbf{N}O_2Ago$	+	$2Cl_2$	=	$4AgCl$	+	$2\mathbf{N}_2O_5$	+	O_2].

The silver salt must be first heated to about 200° F. (93·5° C.) and afterwards kept at 150° F. (65·6° C.) The products are to be condensed in a cold receiver.

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(2.) By passing the vapor of chloride of azotyle over argentic nitrate heated to 140° F. (60° C.)

$$NO_2Cl + AgNO_3 = AgCl + N_2O_5.$$

Chloride of azotyle + Argentic nitrate = Argentic chloride + Nitric anhydride.

$$[\mathbf{N}O_2Cl + \mathbf{N}O_2Ago = AgCl + \mathbf{N}_2O_5].$$

(3.) By adding phosphoric anhydride to nitric acid, thereby dehydrating it, the mixture being afterwards cooled and distilled. (Weber.)

$$6HNO_3 + P_2O_5 = 2H_3PO_4 + 3N_2O_5.$$

Nitric acid + Phosphoric anhydride = Phosphoric acid + Nitric anhydride.

$$[6\mathbf{N}O_2Ho + P_2O_5 = 2\mathbf{P}OHo_3 + 3\mathbf{N}_2O_5].$$

Properties.—A colorless solid, crystallizing in rhombic or in six-sided prisms. It melts at 85° F. (29·5° C.), and boils at 113° F. (45° C.) It is a very unstable body, and is decomposed by a heat of 122° F. (50° C.). Sometimes it explodes spontaneously. It unites energetically with water to form nitric acid, the combination being attended by a great elevation of temperature. A crystalline hydrate ($2N_2O_5$, H_2O, specific gravity 1·642) is formed by dissolving N_2O_5 in strong nitric acid.

Nitric Acid, HNO_3=63 ($\mathbf{N}O_2HO$).

Molecular weight, 63°. *Molecular volume*, |_|_|. *Specific gravity at* 59° F. (15° C.), 1·530. *Relative weight* (H=1) *at* 187° F. = 29·6. 1 *litre of nitric acid vapor weighs* 31·5 *criths*=2·822 *grms.* *In* 100 *parts*=N_2O_5, 85·72, H_2O, 14·28.

Synonyms. *Aqua Fortis* (Alchymists); *Solutive Water* (Geber); *Spirit of Nitre* (Glauber); *Hydric Nitrate; Hydrogen Nitrate* (Watts in Fownes).

History.—Nitric acid was known to the alchymists at a very early period. Priestley (1777) noticed its formation when electrical sparks were passed through air: Cavendish (1785) remarked the acidity of the product when hydrogen was burnt in air, due, as he found, to the formation of nitric acid, the composition of which was thus determined. Davy, Guy Lussac, and Thompson determined the proportions in which nitrogen and oxygen were present in the acid.

Natural History. (*a.*) *In the mineral kingdom* it is found as nitres, soda or cubic nitre being obtained from Chili, and potash or prismatic nitre from India. These are formed by the rapid oxidation of organic nitrogenized bodies, such as urine, etc., under the influence of a tropical heat, and in the presence of soils rich in alkalies. It is also found as nitrates in many well waters, produced by the oxidation of azotized animal matters as they percolate in solution through the soil. Nitrate of ammonia, moreover, is found in rain water, the

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atmospheric electricity effecting the combination of the nitrogen and oxygen, the nitric acid formed combining with ammonia. (*b.*) *In the vegetable kingdom.*—Nitric acid is not found in the recent juices of plants, but it occurs in dried leaves (*e. g.*, in those of tobacco), arising from the decomposition of the alkaloids and the oxidation of their nitrogen. (*c.*) *In the animal kingdom* it is not commonly found except in the urine after the administration of ammonia.

Preparation. (1.) By the direct union of oxygen and nitrogen.

(*a.*) By the passage of sparks through a mixture of two volumes of nitrogen and five volumes of oxygen.

(*b.*) By burning a mixture of one part of nitrogen and ten parts of hydrogen in air or oxygen. The water formed will be found to contain traces of nitric acid.

(2.) By treating nitrous anhydride (N_2O_3) and nitric peroxide (N_2O_4) with water (*see* pages 109 and 112).

(3.) By the slow oxidation of organic matters containing nitrogen or ammonia in the presence of an alkali.

(4.) *Ordinary manufacturing process.*—By the decomposition of potassic or sodic nitrate with strong sulphuric acid. The decomposition is two-fold:—

(*a.*) The sulphuric acid displaces half the nitric acid—

H_2SO_4	+	$2NaNO_3$	=	$NaNO_3$	+	$NaHSO_4$	+	HNO_3.
Sulphuric acid	+	Sodic nitrate	=	Sodic nitrate	+	Hydric sodic sulphate	+	Nitric acid.
[$\mathbf{S}O_2Ho_2$	+	$2\mathbf{N}O_2Nao$	=	$\mathbf{N}O_2Nao$	+	$\mathbf{S}O_2HoNao$	+	$\mathbf{N}O_2Ho$].

(*b.*) By an increased temperature the hydric sodic sulphate decomposes the remaining sodic nitrate, the nitric acid from which distils over—

$NaNO_3$	+	$NaHSO_4$	=	Na_2SO_4	+	HNO_3.
Sodic nitrate	+	Hydric sodic sulphate	=	Sodic sulphate	+	Nitric acid.
[$\mathbf{N}O_2Nao$	+	$\mathbf{S}O_2NaoHo$	=	$\mathbf{S}O_2Nao_2$	+	$\mathbf{N}O_2Ho$].

The sodic nitrate (cubic or Chili nitre) is ordinarily used, as it is *cheaper* than potassic nitrate, and yields *a larger percentage* of nitric acid (*i. e.*, as 85 to 101·1). The sodic sulphate left in the retort is used in glass manufacture. The strongest acid (HNO_3) is obtained by distilling the commercial acid with its own bulk of sulphuric acid.

Impurities.—Lower oxides of nitrogen; chlorine and iodine (derived from the alkaline chlorides and iodides in the nitre); sulphuric acid, iron, alumina, potash, and soda salts.

Preparation of Pure Acid.—Dilute the acid with its own bulk of water; add one grain of potassic bichromate for every 100 grains of the strong acid, in order to oxidize any lower oxides of nitrogen present. Add nitrate of silver to precipitate any chlorine; syphon off the clear liquid and distil, rejecting the first half of the distillate.

Properties.—(*a.*) *Sensible.* When pure, nitric acid is a colorless liquid, but it is more often found in commerce of a yellow color, from

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the presence (by decomposition) of nitrous acid or nitric peroxide. It forms grey fumes when exposed to the air, the acid absorbing water, and condensing into minute drops. Its taste is powerfully acid.

(β.) *Physiological.* It is an intensely irritant poison. Sodic carbonate or magnesia in water should be given as antidotes.

(γ.) *Physical.* Its specific gravity varies according to its strength (*see* Table I. in Appendix). When an acid of any gravity is boiled for some time, an acid of a definite strength is formed ($2HNO_3+3H_2O$). This is the acid of the Pharmacopœia, and has a specific gravity of 1·42.

Action of Heat.—The strong acid (1·5) boils at 210° F. (98·88° C.), and an acid of specific gravity 1·42 at 248° F. (120° C.). At high temperatures it is decomposed ($2HNO_3=2NO_2+H_2O+O$). The strong acid (specific gravity 1·5) freezes at —40° F. (— 40° C.), and an acid of specific gravity 1·4 at — 41° F. (— 40·55° C.), forming in each case a white buttery mass.

Action of Light.—The acid is decomposed by light into nitric peroxide, water and oxygen, the solution becoming more or less colored.

(δ.) *Chemical.* Nitric acid reddens litmus. It is a monobasic acid, forming salts called nitrates, which have the formula $M'NO_3$. It acts as a powerful oxidizing agent, owing to the large amount of oxygen it contains (¾ of its weight), and the ease with which it can part with it. Thus by its action iodine, phosphorus, sulphur, selenium, carbon, boron, and silicon are converted into their highest oxy-acids, whilst the lower oxides, such as sulphurous, arsenious, and phosphorous acids, are at once converted into higher oxides.

Action of Acids.—*Sulphuric acid* has no action upon nitric acid except dehydration. *Hydrochloric acid* decomposes it, forming aqua regia, or nitro-hydrochloric acid (3 of hydrochloric and 1 of nitric acids), a solution containing chlorine and chloride of azotyle or nitrosyle (NOCl) ($HNO_3+3HCl=2H_2O+NOCl+Cl_2$). When aqua regia is heated, it evolves nitric oxide and chlorine, which latter, in the nascent state, dissolves gold and platinum ($2NOCl+2Cl_2+2Au=N_2O_2+2AuCl_3$).

Action on Metals and Metallic Oxides.—It may here be noted that when sulphuric acid acts on metallic zinc, or when hydrochloric acid acts on metallic iron or tin, free hydrogen is evolved:

$$H_2SO_4 + Zn = ZnSO_4 + H_2.$$
$$2HCl + Fe = FeCl_2 + H_2.$$

If sulphuric acid, however, acts on oxide of zinc, or hydrochloric acid acts on oxide of copper, the hydrogen then is not liberated as free hydrogen, but in combination with oxygen, as water:—

$$H_2SO_4 + ZnO = ZnSO_4 + H_2O.$$
$$2HCl + CuO = CuCl_2 + H_2O.$$

When, however, nitric acid acts on metallic zinc or copper, no free hydrogen is evolved, because the oxygen which is liberated at the

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same time, effects, when in the nascent state, the immediate oxidation of the hydrogen. The results, however, produced by the action of nitric acid on the metals vary. It will be noticed that the action of a dilute acid is more intense than that of a strong acid. On *the noble metals* (such as gold, platinum, titanium, and tantalum, etc.) it is without action. On *silver and palladium*, if the acid be dilute, and the liquid kept cold, no gas is evolved, nitrous acid being produced, which remains in solution—($Ag_2 + 3HNO_3 = 2AgNO_3 + H_2O + HNO_2$). On *copper and mercury*, an acid of specific gravity 1·25 evolves nitric oxide (N_2O_2) ($3Cu + 8HNO_3 = 3CuN_2O_6 + 4H_2O + N_2O_2$), but an acid of specific gravity 1·42 evolves nitric peroxide (N_2O_4), ($Cu + 4HNO_3 = CuN_2O_6 + 2H_2O + N_2O_4$); whilst if the mixture of the nitric acid and the metal be heated, pure nitrogen will be disengaged ($5Cu + 12HNO_3 = 5CuN_2O_6 + N_2 + 6H_2O$). On *zinc* (upon which the action of nitric acid is energetic), a dilute acid yields nitrous oxide (N_2O) ($4Zn + 10HNO_3 = 4ZnN_2O_2 + 5H_2O + N_2O$), whilst a stronger acid sets free ammonia, which at once combines with any excess of acid present ($4Zn + 9HNO_3 = 4ZnN_2O_6 + 3H_2O + H_3N$). *Tin and antimony* are oxidized but not dissolved by nitric acid. In the case of tin an insoluble stannic oxide (SnO_2) is formed, called *putty powder*, and nitric peroxide evolved ($Sn + 4HNO_3 = SnO_2 + 2H_2O + 2N_2O_4$).

On *bismuth*, *tin* and *iron* the strong acid (Sp. Gr. 1·5) has no action, but if a little water be added, energetic action at once commences. If iron, after having been immersed in the strong acid is taken out, and, without being wiped, is placed in a weak acid, the iron will be found to have assumed a passive state, that is, the weak acid will have no action upon it.

Heated with an *oxide* or a *metallic base*, nitric acid evolves no gas but forms salts called nitrates ($CuO + 2HNO_3 = H_2O + CuN_2O_6$) all of which are soluble.

Action on Organic Bodies.—Nitric acid destroys all organic bodies; it stains all albuminous substances yellow; when added to morphia, brucia, or narcotine they are turned red; it oxidizes and bleaches indigo (C_2H_5NO), changing it into isatin ($C_2H_5NO_2$). Substitution compounds are often formed by the action of the strong acid on organic bodies (*see* page 113).

Tests. (α.) *In a free state.*

(1.) The production of red fumes by its action on the metals (N_2O_2 + air).

(2.) Its power of reddening morphia and brucia.

(β.) *In a combined state* (as nitrates).

(1.) Add to a nitrate some sulphuric acid to liberate the nitric acid, and float on the mixture a solution of ferrous sulphate. A part of the nitric acid will be reduced, the ferrous becoming ferric sulphate, whilst the remainder of the ferrous sulphate solution will absorb the lower oxides of nitrogen set free, and the solution become brown at the junction of the two liquids. (Liebig.)

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(2.) Add to a solution of a nitrate, sulphuric acid and a little indigo solution; the latter will be bleached by the nitric acid liberated by the action of the sulphuric acid on the salt.

(3.) By adding sulphuric acid to a nitrate and shaking the mixture up with mercury, N_2O_2 is set free, the quantity indicating the amount of nitric acid present (Crum's test modified by Frankland).

(4.) A nitrate placed on red-hot charcoal deflagrates (Chlorates act similarly).

Uses. (*a.*) *In nature* nitric acid is one of the sources of the nitrogen of plants. It is of no special use to animals. (*b.*) *In chemistry and in the arts* its chief use is as a solvent and an oxidizer. (*c.*) *In medicine* we have in the B.P. the *acidum nitricum* (specific gravity 1·42, and containing 70 per cent. of HNO_3, being in reality $2HNO_3,3H_2O$) and *acidum nitricum dilutum* (Sp. Gr. 1·101), containing 17·44 per cent. of HNO_3. The strong acid (Sp. Gr. 1·5) is used as an escharotic.

Compounds of Nitrogen and the Haloids.

The combination of nitrogen with the haloids cannot be effected directly, whilst there is some doubt as to whether any such compounds exist without the presence of hydrogen.

1. *Nitrogen and Fluorine.*

No compound of nitrogen with fluorine is known without hydrogen (NH_4F).

2. *Nitrogen and Chlorine.*

Chloride of Nitrogen (*Nitrous Chloride*).

Of the composition of this body there is considerable doubt, its analysis being exceedingly difficult, owing to its explosive nature. Some regard it as NCl_3, and others as a compound of $NHCl_2$ and NCl_3. In the former case it is regarded as an ammonia molecule, where three atoms of hydrogen are replaced by three of chlorine; in the latter as a double ammonia molecule, where five hydrogens are replaced by five chlorines, one hydrogen not being disturbed. Possibly there may be a series of these compounds, such as NH_2Cl—$NHCl_2$—NCl_3.

History.—Discovered by Dulong in 1812; investigated by Davy.

Preparation.—By the action of chlorine on a strong solution of ammonic chloride.

NH_4Cl	+	$3Cl_2$	=	$4HCl$	+	NCl_3.
Ammonic chloride	+	Chlorine	=	Hydrochloric acid	+	Chloride of nitrogen.
[**N**H_4Cl	+	$3Cl_2$	=	$4HCl$	+	**N**Cl_3].

Note.—The action of chlorine on an *excess* of ammonia is to set free nitrogen ($8NH_3+3Cl_2=6NH_4Cl+N_2$). When ammonia gas burns in chlorine, hydrochloric acid and nitrogen are formed.

Properties. (*a.*) *Sensible.*—An oily liquid (like olive oil) having a peculiar odor and very irritating to the eyes and nose.

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(β.) *Physical.*—Specific gravity 1·653. It is volatile at ordinary temperatures, and boils at 160° F. (71·1° C.). It does not freeze at —16·6° F. (—27° C.) It explodes violently at from 200° to 212° F. (93° to 100° C.)

(γ.) *Chemical.*—The elements in chloride of nitrogen are very feebly combined. The mere contact of phosphorus, sulphur, arsenic, the alkalies, or of inflammable bodies generally, such as turpentine, etc., cause its immediate explosion. The metals, the mineral acids, alcohol, and water have no action upon it.

3. *Nitrogen and Bromine.*

It is doubtful whether any compound of these bodies exists. Millon in 1828 remarked that potassic bromide decomposed nitrous chloride (NCl_3) forming a red liquid having very similar properties to the chloride of nitrogen. He considered that the Cl_3 had been replaced by Br_3.

4. *Nitrogen and Iodine.*

Iodide of Nitrogen.

Of the composition of this body there is much doubt. It was formerly represented by the formula NI_3; Gladstone and Frankland regard it as NHI_2 (nitrous hydrodiniodide), and Bunsen as NI_3+NH_3. Possibly there is a series of these compounds.

Preparation.—By the action of iodine on ammonia.

$3NH_3 + 2I_2 = NHI_2 + 2NH_4I.$

Ammonia + Iodine = Nitrous hydrodiniodide + Ammonic iodide.

$[3\mathbf{N}H_3 + 2I_2 = \mathbf{N}HI_2 + 2\mathbf{N}H_4I]$. (Frankland).

NOTE.—Nitrogen is liberated by the action of chlorine and bromine (but not by the action of iodine) on ammonia.

Properties.—A black powder having an iodine smell and a very high specific gravity. It is easily decomposed when dry by heat or by the touch of a feather, fumes of iodine vapor being liberated ($NHI_2=N+HI+I$). *Water* dissolves and decomposes it, forming an ammonic iodate, iodine with a little free nitrogen being evolved. *Sulphuretted hydrogen* decomposes it, forming ammonic iodide, hydriodic acid, and sulphur ($NHI_2+2H_2S=H_4NI+HI+S_2$). It is also decomposed by solutions of the alkalies and of the alkaline earths, iodides and iodates being formed.

COMPOUNDS OF NITROGEN, OXYGEN, AND CHLORINE.

Nitrous Oxychloride. NOCl=65·5($\mathbf{N}$OCl).

Molecular weight, 65·5. *Molecular volume*, $\boxed{\ |\ |\ }$. *Relative weight*, 32·75. *Specific gravity, theoretic*, 2·2663. 1 *litre weighs* 32·75 *criths*=2·9344 grms.

Synonyms.—*Chloro-nitrous gas* (Frankland); *Nitrosyle chloride* (Bloxam); *Azotyle chloride.*

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Preparation. (1.) By mixing together two volumes of nitric oxide (N_2O_2) and one volume of chlorine. The three volumes condense to one volume.

(2.) By heating a mixture of nitric and hydrochloric acid (aqua regia).

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$
Nitric acid + Hydrochloric acid = Nitrous oxychloride + Chlorine + Water.

$$[\mathbf{N}O_2Ho + 3HCl = \mathbf{N}OCl + Cl_2 + 2\mathbf{O}H_2].$$

Properties.—An orange-colored gas becoming a red liquid at 0° F. (—18° C.), which boils at 32° F. (0° C.) It is decomposed in the presence of mercury, or by contact with water. If passed into sulphuric acid cooled to 32° F. (0° C.), crystals of $NOHSO_4$ are deposited ($NOCl + H_2SO_4 = HCl + NOHSO_4$).

Nitrylic Chloride ($NO_2Cl = 81{\cdot}5$) ($\mathbf{N}O_2Cl$).

Relative weight (H=1), 40·75. *Specific gravity of the liquid*, 1·32; *of the vapor*, 2·63 (*theoretic*, 2·819).

Synonyms.—*Chloride of Nitryl*—*Nitric Dioxychloride* (Frankland); *Chloropernitric gas* (Frankland).

Preparation. (1.) By the action of phosphoric oxytrichloride on plumbic or argentic nitrate.

$$3AgNO_3 + PCl_3O = Ag_3PO_4 + 3NO_2Cl.$$
Argentic nitrate + Phosphoric oxytrichloride = Argentic phosphate + Nitrylic chloride.

$$[3\mathbf{N}O_2Ago + \mathbf{P}OCl_3 = \mathbf{P}OAgo_3 + 3\mathbf{N}O_2Cl].$$

(2.) By the action of chlor-hydrosulphuric acid on potassic nitrate.

Properties.—A yellow liquid boiling at 41° F. (5° C.) and not freezing at —24° F. (—31° C.) It is decomposed by water, nitric and hydrochloric acids being formed ($NO_2Cl + H_2O = HCl + HNO_3$).

Chloro-Nitric Gas, $NOCl_2$ or $N_2O_2Cl_4$ ($'\mathbf{N}^{IV}_2O_2Cl_4$).

Synonyms.—*Nitric dioxy-tetrachloride* (Frankland); *Nitric oxy-dichloride*; *Azotyle bichloride*.

Preparation.—Formed, together with nitrous oxychloride, by heating aqua regia.

$$2HNO_3 + 6HCl = N_2O_2Cl_4 + 4H_2O + Cl_2.$$
Nitric acid + Hydrochloric acid = Chloro-nitric gas + Water + Chlorine.

$$[2\mathbf{N}O_2Ho + 6HCl = {}'\mathbf{N}^{IV}_2O_2Cl_4 + 4\mathbf{O}H_2 + Cl_2].$$

Properties.—Below 19° F. (—7° C.) it is a red liquid, but above this temperature a yellow gas. It is decomposed by water or by an alkaline hydrate. It forms with mercury, nitric oxide and mercurous chloride ($4Hg + N_2O_2Cl_4 = 2Hg_2Cl_2 + N_2O_2$).

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CHAPTER VI.

PHOSPHORUS.

PHOSPHORUS. Compounds of Phosphorus and Oxygen—Suboxide of Phosphorus—Hypophosphorous acid—Phosphorous anhydride—Phosphorous acid—Phosphoric anhydride—Metaphosphoric acid—Pyrophosphoric acid—Orthophosphoric acid—Compounds of Phosphorus and the Haloids—Phosphorous Chloride—Phosphoric Chloride—Phosphoric Oxy-trichloride—Phosphoric Sulpho-trichloride—The Iodides of Phosphorus—Phospham—Action of Ammonia on Phosphorus Compounds.

PHOSPHORUS (P = 31).

Atomic weight, 31. *Molecular weight* (31 × 4), 124. *Atomic volume* $\square$ *or* $\frac{1}{2}$. *Molecular volume* $\square\!\square$. *Atomicity pentad* (v) *and triad* (‴) (*as in* PCl_5; PH_4I; PH_3; PCl_3.) *Relative weight* (H=1), 62. *Specific gravity of vapor*, 4·2904. 1 *litre of P. vapor weighs* (62 *criths*, *not* 31 *criths*) 5·555 *grms.*

The name *phosphorus* (φῶς and φέρω), equivalent to the Latin name of *lucifer*, is derived from its property of shining in the dark. The name had been previously given to various other bodies that were luminous when heated, viz., *Baldwin's phosphorus* (calcic nitrate), *Bolognian phosphorus* (baric sulphate), *Homberg's phosphorus* (fused calcic chloride), etc.

History.—Phosphorus was accidentally discovered by Brandt in urine during certain alchemical investigations (1669.) He showed some to a German chemist, Kunkel, who spoke of it to his friend Kraft. Kraft bought the secret of its preparation from Brandt for 200 dollars. Kunkel (1674) afterwards made it in sufficient quantity for sale, the material being known as "Kunkel's phosphorus." Boyle and his assistant, Godfrey Hankwitz (1680), also prepared it, the latter selling it under the name of "English Phosphorus." The process was improved by Margraaf (1740). Gahn, in 1768, discovered phosphorus in bones, and Scheele (1769) invented a ready process for preparing it therefrom, which was afterwards perfected by Fourcroy, Vauquelin, Nicholas, and Pelletier.

Ancient theories as to its nature.—Phosphorus was believed by the Stahlians (their theory being in vogue at the time of its discovery) to be a compound of phlogiston and of the white fumes produced by its combustion, which were believed by Stahl to be muriatic acid. Margraaf, of Berlin, in 1740, proved that this was an error, and that the white flakes were phosphoric acid. The Stahlians then asserted that phosphorus was a compound of phosphoric acid and phlogiston. In 1772, Guyton Morveau proved that the phosphoric acid from burn-

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ing phosphorus was heavier than the phosphorus from which it was obtained; after which Lavoisier, in 1774-5, made his famous experiment of burning a known weight of phosphorus in a known quantity of oxygen, by which he proved phosphoric acid to be a compound of oxygen and phosphorus. In 1810-12, Davy, Gilbert, Guy Lussac, and Thénard, established its elementary nature, since which time its various allotropes have been discovered.

Natural History.—Phosphorus is never met with in nature in an uncombined state.

(α.) In the *mineral kingdom* it is found in all the primitive and volcanic rocks (chiefly as $Ca_3,2PO_4$), and also in the soils produced by their disintegration. It occurs as apatite and coprolites (phosphate of lime), also as wavellite and massive phosphate of alumina, lead, uranium, etc. (β.) In the *vegetable kingdom* phosphorus is extracted from the soil by plants for animal use. It is found in all parts of the vegetable, but more particularly in the seed.

Quantity of Phosphoric anhydride per cent. present in different substances.

	P_2O_5 per cent.
Ash of tobacco stalk	2·73
,, straw (barley, wheat, oats, &c.)	3·00
,, turnips	6·10
,, clover	6·30
,, flax	10·77
,, potatoes	11·30
,, oats	14·90
,, wheat	16·40

(γ.) In the *animal kingdom* phosphorus is found in considerable quantities in brain and in nerve tissue, as though it were essential to the exercise of the higher functions. It is found in all the secretions in urinary and in other calculi, in the tartar of the teeth thrown down from the saliva by the ammonia of the breath, etc.

Proportions of Phosphorus per cent. present in various animal tissues.

		Phosphorus per cent.
Mulder.	Dry fibrin	0·32—0·42.
	,, egg albumen ..	
	,, blood ,, ..	0·33.
Lassaigne.	Brain normal ..	1·93—1·97.
Courbe.	,, of idiots ..	1·00—1·50.
	,, of sane ..	2·00—2·50.
	,, of madmen ..	3·00—4·50.

Bone .. .. .. 16·96 P. = 53 per cent. $Ca_3P_2O_8$.
Solid matters of urine 2·32 per cent. of alkaline and earthy phosphates.

Preparation.—Phosphorus is the only element in the preparation of which animal substances are employed.

(1.) Preparation from urine (*old methods.*)

1*st process.*—Evaporate the urine to dryness; mix the residue with sand and distil. The silica liberates the phosphoric acid which the carbon reduces. (Boyle and Hankwitz.)

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2nd process.—Precipitate the urine with plumbic acetate; mix the precipitate with one-fourth its weight of charcoal, and distil. (Grobert.)

(2.) Preparation from native calcic phosphate and from bones. (New process of Scheele as modified by Vauquelin, Nicholas, etc.)

(α.) Bones (from which the gelatine may be previously extracted) are heated in an open fire to whiteness, whereby "bone-earth" Ca_32PO_4 ($\mathbf{P}_2O_2Cao''_3$) is obtained.

(β.) Three parts of this bone-earth are now digested for several days with a mixture of 2 parts of strong sulphuric acid (Sp. Gr. 1·55), and 18 to 20 parts of water. An insoluble sulphate of lime and a soluble monocalcic salt called "superphosphate" are thus formed:—

$$Ca_32PO_4 + 2H_2SO_4 = 2CaSO_4 + Ca2H_2PO_4.$$

Tricalcic phosphate (bone ash) + Sulphuric acid = Calcic sulphate + Calcic superphosphate.

$$[\mathbf{P}_2O_2Cao''_3 + 2\mathbf{S}O_2Ho_2 = 2\mathbf{S}O_2Cao'' + \mathbf{P}_2O_2Ho_4Cao''].$$

(γ.) The mixture is now filtered through horsehair to remove the calcic sulphate.

(δ.) The clear filtrate is now evaporated to a syrup, which is then mixed with one-fourth its weight of charcoal and heated, whereby water is expelled, and an intimate mixture of charcoal and metaphosphate of lime formed:—

$$Ca2H_2PO_4 = Ca2PO_3 + 2H_2O.$$

Calcic superphosphate = Calcic metaphosphate + Water.

$$[\mathbf{P}_2O_2Ho_4Cao'' = \mathbf{P}_2O_4Cao'' + 2\mathbf{O}H_2].$$

(ε.) This mixture is now distilled at a red heat in an earthenware retort rendered air-tight with borax and sandy clay, when phosphorus passes over and is collected under hot water:—

$$3Ca2PO_3 + 10C = Ca_32PO_4 + 10CO + P_4.$$

Calcic metaphosphate + Carbon = Tricalcic phosphate + Carbonic oxide + Phosphorus.

$$[3\mathbf{P}_2O_4Cao'' + 10C = \mathbf{P}_2O_2Cao''_3 + 10\mathbf{C}O + P_4].$$

Wohler recommends using sand and charcoal, whereby the whole of the phosphorus may be obtained. Thus:—

$$3Ca2PO_3 + 18C + 3SiO_2 = 3CaSiO_2 + 18CO + P_6.$$

Calcic metaphosphate + Carbon + Silica = Calcic silicate + Carbonic oxide + Phosphorus.

$$[3\mathbf{P}_2O_4Cao'' + 18C + 3\mathbf{Si}O_2 = 3\mathbf{Si}Cao'' + 18\mathbf{C}O + P_6.]$$

(ζ.) The phosphorus is purified first by washing it under hot water containing bleaching powder; then by fusion under ammonia to remove any *acid impurities*, and finally under a mixture of sulphuric acid and potassic dichromate, whereby any *suboxide of phosphorus* present is oxidized and changed into soluble phosphoric acid. The pure phosphorus is then strained through leather under hot water, and cast into sticks.

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(3.) Phosphorus may also be prepared by passing a stream of hydrochloric acid gas over a mixture of charcoal and heated bone ash.

$$Ca_3 2PO_4 + 6HCl + 8C = 3CaCl_2 + 8CO + 3H_2 + P_2.$$

Tricalcic phosphate + Hydrochloric acid + Carbon = Calcic chloride + Carbonic oxide + Hydrogen + Phosphorus.

$$[\mathbf{P_2O_2}Cao''_3 + 6HCl + 8C = 3\mathbf{Ca}Cl_2 + 8\mathbf{C}O + 3H_2 + P_2].$$

Varieties. — Phosphorus assumes different allotropic forms, of which, amongst others, are the following :—

1. *Clear transparent variety.*—This is a yellow, soft, wax-like body, tasteless in the solid form, but having a sharp, pungent flavour in solution. It has the odour of garlic. Its specific gravity varies from 1·848 to 1·853. It is a non-conductor of heat. It volatilises at 111·2° F. (44° C.), the fumes in a dark room appearing luminous.

2. *White opaque variety* (Rose).—This is formed by the action of light on the above, when kept under water. The white opaque crust forms most readily when the water contains an abundance of calcareous matter. Specific gravity, 1·515.

3. *Black variety* (Thénard) is produced when the common phosphorus is melted and suddenly cooled to 32° F. (0° C.).

4. *Red variety* (Schrötter) is formed by heating yellow phosphorus for thirty or forty hours in an atmosphere in which it cannot oxidise, at a temperature of from 460° to 478° F. (238° to 248° C.). It is amorphous, and of a dull red color, without taste, odor, or action on the body. Its specific gravity is 2·14, and it fuses at 550·4° F. (288° C.) It is not luminous until heated to its firing point (600·8° F. (316° C.)). It is insoluble in carbonic bisulphide. It is changed back again to the common yellow variety by the action of heat in the presence of air. It is permanent in the air, and gives off no vapor. It is not fired by contact with iodine.

Properties.—(α.) *Sensible.*—A solid. The yellow variety may be prepared in octahedral or dodecahedral crystals by evaporating its solution in carbonic disulphide in an atmosphere of carbonic anhydride. The red variety is amorphous. The *color* varies. The common variety is yellow; Rose's, white, like porcelain; Thénard's, black; and Schrötter's, red. The *odor* of all the varieties, excepting that of Schrötter, is said to be like garlic. Its *taste*, except Schrötter's variety, is acrid.

(β.) *Physiological.*—All varieties (except the red phosphorus) are active poisons, less than half a grain having proved fatal. Its exact physiological action is doubtful, some considering that its poisonous action is due to its oxidation internally at the expense of the oxygen of the blood; whilst others hold that it is a true blood poison, and remains unaltered by absorption. To get it out of the system by the stomach-pump, or, if after an interval, by an emetic, administering at the same time some thick gruel containing chalk or magnesia, the former to suspend the particles, and the latter to neutralise any acid

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products formed, constitutes the best method of treatment in cases of poisoning. Above all, the administration of oils or fatty matters must be avoided. The red variety is not poisonous. The vapours, when inhaled (as in lucifer-match making), produce disease of the jaw bone.*

(γ.) **Physical.**—*Specific Gravity.*—This varies: the specific gravity of the *yellow* variety is 1·848 to 1·853; of the *white*, 1·515; and of the *red*, 2·14. The *specific gravity of the vapor* is 4·303; that is, its volume is 62 times the weight of the same volume of hydrogen at the same temperature and pressure. Theoretically, it should be only 31 times its weight. Its atom, therefore, is one-half the size of the hydrogen atom.

Action of Heat.—The yellow variety melts and fires at about 112° F. (44·6° C.). When melted under a solution of potassic hydrate it may be cooled to 90° F. (32° C.) without solidifying; but if, whilst in this state, it be touched under the solution with a solid point, it immediately solidifies, and the temperature rises to 112° F. (44·5° C.). It volatilizes at ordinary temperatures in moist air, and at 217° F. (103° C.) in dry air, giving off an alliaceous odor. It boils or distils at 554° F. (290° C.), but when boiled in water, phosphorus vapor comes over along with the watery vapor at 212° F. (100° C.).

If the yellow variety be heated a little *above* its melting point, and suddenly cooled, it forms the black or Thénard's phosphorus; this variety may, however, be changed back again to the yellow form by fusion and slow cooling. If the yellow variety be heated *nearly*, but not quite to its boiling point, and suddenly cooled, it becomes viscous. If the yellow phosphorus be heated for a long time at from 460° F. (238° C.), to 480° F. (249° C.), in hydrogen, or in nitrogen, or in any atmosphere in which it cannot fire, it forms the red variety or "Schrötter's phosphorus," which by a heat of 500° F. (260° C.) may be again reconverted into the yellow variety. Rose's, or the white phosphorus, at a heat of 122° F. (50° C.), becomes the ordinary yellow phosphorus.

Action of Light.—When yellow phosphorus is exposed under water to *diffuse daylight*, it changes to the white porcelain variety (Rose's). *Sunlight* acting on common phosphorus preserved either under water or in a vacuum, changes it to an orange-yellow color. (Napoli).

Action of Electricity.—Phosphorus is a bad conductor of electricity, unless it be melted.

Solubility.—The solubility of phosphorus in different liquids is represented in the following table:—

Solubility of Phosphorus in various Liquids.

Water	Slight.
Strong Acetic acid	0·04 per cent.
Alcohol (Sp. Gr. 834) ..	0·4 ,,
Ether (Sp. Gr. 758)	0·9 ,,
Olive oil (Sp. Gr. 916) ..	1·0 ,,
Turpentine (Sp. Gr. 996) ..	2·5 ,,
Carbon Bisulphide	10 to 15 times its weight.

* See Woodman's and Tidy's "Forensic Medicine," p. 73.

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The solutions, however, differ in strength very materially, according to the length of time that the solvent has acted.

Table showing the Solubility of Phosphorus in various Liquids after remaining in contact with them for different times.

Liquid.	Quantity by Measure.		Quantity by Weight.	Amount of Phosphorus taken up during					
				1st day.	2nd day.	3rd day.	4th day.	5th day.	6th day.
Alcohol	1 oz.	=	400 grs.	0·31	0·42	0·54	0·96	1·5	1·6
Ether	1 oz.	=	364 ,,	2·9	3·0	3·1	3·3	3·3	3·3
Olive oil	1 oz.	=	440 ,,	1·0	1·3	2·4	3·0	4·0	4·4
Turpentine ..	1 oz.	=	478 ,,	3·1	4·8	6·5	8·6	10·0	12·0

When the hydrogen flame containing phosphorus is examined by the spectroscope, two green lines are apparent.

(δ.) *Chemical.*—Our remarks, for the present, refer to the ordinary yellow variety only. Phosphorus has an intense affinity for oxygen. *Phosphoric acid* is produced by its rapid combustion, and *phosphorous acid* by its slow combustion, in dry air or oxygen. (*See* Analysis of Air, p. 97.) In moist air the fumes evolved from phosphorus are luminous in the dark. They are said to consist of ammonic nitrate, formed by the action of ozonised oxygen on the air, and aqueous vapor.

This slow combustion of phosphorus is influenced by many circumstances:

(1.) Phosphorus is not luminous in pure oxygen at a temperature below 60° F. (15·6° C.).

(2.) The presence of a diluting gas, such as hydrogen, nitrogen, etc., greatly reduces the temperature at which phosphorus becomes luminous.

(3.) It is essential that moisture should be present.

(4.) The luminosity is greatly promoted by heat, and checked by cold. It is not luminous in air at 32° F. (0° C.), and but faintly luminous at from 41° to 43° F. (5° to 6° C.); but above this the luminosity is in direct ratio to the heat applied.

(5.) The luminosity is increased by rarefaction; whilst on the contrary, a pressure of 4 atmospheres entirely checks it.

(6.) The luminosity is stopped by the presence of certain gases and vapors. In addition to those mentioned in the following table, we may also name bromine, iodine, nitrous oxide, nitric oxide, vapors of alcohol and of volatile oils, etc., as interfering with its slow combustion.

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Proportions in which certain Gases stop the slow Combustion of Phosphorus in air at ordinary Temperatures and Pressures.

Name of the Gas.	Proportions in the air by volume.	Temperature when the luminosity ceases.	
		F.	C.
Sulphuretted hydrogen	$\frac{1}{9}$	66·0	18·9
Sulphurous acid	$\frac{1}{11}$	44·9	7·2
Chlorine	$\frac{1}{12}$	53·9	12·2
Do.	$\frac{1}{25}$	65·8	18·8
Ether	$\frac{1}{150}$	65·8	18·8
Olefiant gas	$\frac{1}{450}$	65·8	18·8
Phosphoretted hydrogen	$\frac{1}{1000}$	65·8	18·8
Naphtha	$\frac{1}{1820}$	65·8	18·8
Oil of turpentine	$\frac{1}{4444}$	65·8	18·8
Bisulphide of carbon	Merest trace.	97·0	36·1

Quantities of Vapour required to check the Luminosity of Phosphorus in air at elevated Temperatures.

Gas, or Vapour.	Proportions in the air by volume.	Temperature at which Oxidation ceases.	
		F.	C.
Olefiant gas	$\frac{1}{2}$	199·9	93·3
Ether	$\frac{1}{2}$	214·1	101·2
Do.	$\frac{2}{3}$	219·9	104·4
Naphtha	$\frac{1}{112}$*	169·8	76·6
Turpentine	$\frac{1}{156}$*	185·9	85·5

The oxidation of phosphorus in air, at ordinary temperatures, may be so rapid that it will take fire, more particularly if the phosphorus be in a finely divided state. We may note that phosphorus flames do not spread, owing to the phosphoric acid generated as the product of combustion, collecting on neighbouring objects. Phosphorus combines with nascent hydrogen to form phosphoretted hydrogen.

Action of Water.—Phosphorus does not form a hydrate with water, but when preserved for some time under water, it forms phosphorous acid and phosphoretted hydrogen ($P_2 + 3H_2O = H_3PO_3 + PH_3$).

Action of Haloids.—The haloids attack phosphorus instantly. If iodine and phosphorus be brought into contact, they at once ignite. Brodie has shown that if a little iodine be added to yellow phosphorus, melted in an atmosphere of carbonic anhydride, it will convert an almost unlimited quantity of the yellow into the red amorphous variety. This result depends on the formation of an iodide of phosphorus, the phosphorus of which compound is amorphous. This iodide is decomposed as soon as formed by the yellow phos-

* With a large amount of naphtha and turpentine, phosphorus may be actually distilled without firing.

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phorus to make more iodide, which is again decomposed, and so the action proceeds indefinitely, the whole of the yellow ultimately becoming the red variety.

Phosphorus combines *with sulphur and selenium*, and also *with the metals* (gold and platinum not excepted) by heat. A platinum dish, when constantly used for igniting organic substances containing phosphates, becomes rough. The presence of phosphorus in iron or copper, effects considerable alteration in their properties.

Action on Metallic Solutions.—Phosphorus reduces the salts of many of the metals, such as those of gold, silver, copper, platinum, etc., but it has no action on the salts of lead, iron, zinc, antimony, arsenic or manganese.

Action of Acids.—*Hydrochloric acid* has no action on phosphorus, either hot or cold. When *sulphuric acid*, which has no action on phosphorus in the cold, is heated, the acid is decomposed ($3H_2SO_4 + P_2 = 2H_3PO_3$ (*phosphorous acid*) $+ 3SO_2$). *Sulphurous acid* is also decomposed by it; *nitric acid* oxidises it, phosphoric acid being formed, and the lower nitrogen oxides evolved ($6HNO_3 + P_2 = 2H_3PO_4$ (*phosphoric acid*) $+ 2N_2O_4 + N_2O_2$).

Action of Alkalies and Alkaline Earths. — When phosphorus is heated in contact with the alkalies and alkaline earths, it forms hypophosphites, phosphides, phosphates, etc. If the vapour of phosphorus be passed over lime heated to redness, a chocolate red powder is formed which consists of a mixture of calcic phosphide and calcic pyrophosphate :—

$14P$	$+ 14CaO =$	$2Ca_2P_2O_7$	$+$	$5Ca_2P_2$.
Phosphorus	+ Lime =	Calcic pyrophosphate	+	Calcic phosphide.
[$14\mathbf{P}$	$+14\mathbf{Ca}O =$	$2\mathbf{P}_2O_3Cao''_2$	$+$	$5\mathbf{P}_2Ca_2$].

If phosphorus be boiled with caustic soda or potash, phosphoretted hydrogen is evolved, and a hypophosphite is formed.

$3KHO$	$+$	P_4	$+$	$3H_2O$	$=$	$3KH_2PO_2$	$+$	PH_3.
Potassic hydrate	+	Phosphorus	+	Water	=	Potassic hypophosphite	+	Phosphoretted hydrogen.
$3\mathbf{O}KH$	$+$	P_4	$+$	$3\mathbf{O}H_2$	$=$	$3\mathbf{P}OH_2Ko$	$+$	PH_3.

Heated to redness with sodic carbonate, phosphorus liberates carbon.

Phosphorus has no action on dead mucous membrane, unless freely exposed to the air, when the phosphorus softens, discolors, and in time dissolves it.

The red variety is not characterised by any of the reactions already described. It is singularly negative in its chemical properties.

Tests.—1. *Its Odor.*—This may be recognised in very dilute solutions.

2. *Its property of Fuming in Air and Shining in the Dark.*—These effects are only manifest when the phosphorus is examined either in the dry state, or in solution in water, vinegar, or in the fixed oils, the effects being intensified by the application of heat. It is not manifest when it is dissolved in ether, carbon disulphide, alcohol, turpentine, or in the volatile oils, until the solvent has completely evaporated.

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3. *Its Faculty of Evolving Ozone, etc., in Damp Air.*—This may be known by—

(α.) A solution of argentic nitrate on white paper becoming black.

(β.) Starch and potassic iodide on white paper becoming blue.

(γ). Litmus paper being first reddened and afterwards bleached.

(δ.) The protosalts of manganese being discolored.

4. *The Color of the Flame and the Products of its Combustion.*

5. *Its Action on certain Metallic Compounds.*

(α.) Solid phosphorus reduces metallic gold, silver, copper, etc., from solutions of their salts.

(β.) *Argentic Nitrate* gives a *black* precipitate, with a solution of phosphorus; cupric *sulphate* a *brown* precipitate; and *mercuric chloride* a *yellow* precipitate.

6. *Its Conversion into Phosphoric Acid.*—Boil the phosphorus in a retort with twelve or fourteen times its weight of dilute nitric acid (Sp. Gr. 1·200). Evaporate the solution nearly to dryness, and dissolve the residual phosphoric acid in water. To this solution the tests proper to phosphoric acid must be applied.

Uses.—*In Nature* phosphorus appears essential to plants and animals. It is found abundantly in brain tissue, and more particularly in the sexual organs of both plants and animals. *In the Arts* its principal use is for lucifer matches, in the manufacture of which the phosphorus is mixed with nitre on the Continent, forming "silent matches," and with potassic chlorate in England, forming "detonating matches." The use of the red phosphorus in match-making is becoming extensive. *In Medicine* phosphorus acts as a nervine tonic and aphrodisiac. It is given in skin diseases, low fevers, phthisis, etc. (*Oleum Phosphoratum*, B.P., 12 grs. in 4 fluid ounces of dried almond oil; *Pilula Phosphori*, B.P., phosphorus in balsam of tolu and yellow wax.)

Compounds of Phosphorus and Oxygen.

Oxides or Anhydrides.	Formula.	+ Water ^{n}	= Acids of Phosphorus.	Constitutional formula for Acids.	Name of Acids.
Suboxide of phosphorus	P_4O (?)				
			H_3PO_2	or POH_2Ho	Hypophosphorous acid.
Phosphorous anhydride	P_2O_3 or $\mathbf{P_2O_3}$	$+3H_2O$	$=2H_3PO_3$ or H_3PO_3	or $POHHo_2$	Phosphorous acid.
Phosphoric anhydride	P_2O_5 or $\mathbf{P_2O_5}$	$+ H_2O$	$=H_2P_2O_6$ or HPO_3	or PO_2Ho	Metaphosphoric acid.
Do.	do.	$+2H_2O$	$=H_4P_2O_7$	or $P_2O_3Ho_4$	Pyrophosphoric acid.
Do.	do.	$+3H_2O$	$=H_6P_2O_8$ or H_3PO_4	or $POHo_3$	Orthophosphoric acid, or Phosphoric acid.

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It will be noted from the above table—

1. That there is no anhydride of hypophosphorous acid.

2. That phosphoric anhydride forms three acids by combination with 1, 2, or 3 molecules of water respectively.

3. That although hypophosphorous acid (H_3PO_2), phosphorous acid (H_3PO_3), and common phosphoric or orthophosphoric acid (H_3PO_4) severally contain 3 atoms of hydrogen in the molecule, nevertheless they differ as follows:—

In (α) *Hypophosphorous acid* only 1 hydrogen can be [replaced by a metal (Monobasic.)

In (β) *Phosphorous acid* only 2 hydrogens ditto (Bibasic.)

In (γ) *Phosphoric acid* all 3 ditto ditto (Tribasic.)

Suboxide of Phosphorus (P_4O).

This compound is supposed to constitute the colored residue left after the combustion of phosphorus in air. The deposit thus formed has generally been regarded as a mixture of red phosphorus and a little phosphoric acid. It is also formed by mixing phosphorus with phosphorous chloride, exposing the mixture to air, and afterwards boiling in water. It is a yellow body, becoming red at high temperatures, and igniting when heated. It is insoluble in water, without smell or taste, and without acid or alkaline properties. There is much doubt, however, as to its real nature.

Hypophosphorous Acid, H_3PO_2 ($\mathbf{P}OH_2Ho$).

The anhydride of this acid has never been obtained.

Preparation.—1. (α.) A baric hypophosphite must be first prepared by boiling phosphorus in a solution of baric hydrate (Rose):—

$$3BaH_2O_2 + 2P_4 + 6H_2O = 3(Ba2H_2PO_2) + 2H_3P.$$

Baric hydrate + Phosphorus + Water = Baric hypophosphite + Phosphoretted hydrogen.

$$[3\mathbf{Ba}Ho_2 + 2P_4 + 6\mathbf{O}H_2 = 3\mathbf{P}_2O_2H_4Bao'' + 2\mathbf{P}H_3].$$

(β.) The insoluble baric hypophosphite must be then decomposed with sulphuric acid, whereby hypophosphorous acid is set free:—

$$3(Ba2H_2PO_2) + 3H_2SO_4 = 3BaSO_4 + 6H_3PO_2.$$

Baric hypophosphite + Sulphuric acid = Baric sulphate + Hypophosphorous acid.

$$[3\mathbf{P}_2O_2H_4Bao'' + 3\mathbf{S}O_2Ho_2 = 3\mathbf{S}O_2Bao'' + 6\mathbf{P}OH_2Ho].$$

2. By decomposing plumbic hypophosphite with sulphuretted hydrogen:—

$$(Pb2H_2PO_2) + H_2S = PbS + 2H_3PO_2.$$

Plumbic hypophosphite + Sulphuretted hydrogen = Plumbic sulphide + Hypophosphorous acid.

$$[\mathbf{P}_2O_2H_4Pbo'' + \mathbf{S}H_2 = \mathbf{Pb}S + 2\mathbf{P}OH_2Ho].$$

Properties.—Hypophosphorous acid may be obtained as a thick viscid liquid by careful evaporation under the receiver of an air-pump.

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It has a strong acid reaction. When heated it is decomposed, yielding phosphoric acid and phosphoretted hydrogen ($2H_3PO_2 = H_3PO_4 + H_3P$). It rapidly oxydizes by exposure to air, forming phosphoric acid ($H_3PO_2 + O_2 = H_3PO_4$). It acts as a powerful reducing agent on salts of gold, mercury, etc.

Hypophosphorous acid may be known from phosphorous acid by adding cupric sulphate to the free acid and heating the solution to 131° F. (55° C.). With *hypophosphorous acid* a reddish black precipitate of cupric hydride (Cu_2H_2) is thrown down, which, when heated in the liquid to 212° F. (100° C.), is decomposed with the deposition of the metal and the evolution of hydrogen. With *phosphorous acid*, the metal is precipitated and hydrogen is evolved, but no Cu_2H_2 is formed. Further, hypophosphorous acid reduces the permanganates immediately, but phosphorous acid only after some time. When hypophosphorous acid is treated with zinc and sulphuric acid, it is converted into phosphoretted hydrogen.

Although the acid contains three atoms of hydrogen, it is nevertheless monobasic. Thus it forms salts as follows :—

(α.) Salts of monads — $M'H_2PO_2$, *e.g.*, $K'H_2PO_2$.

(β.) Salts of dyad metals — $M''2H_2PO_2$, *e.g.*, $Ba''2H_2PO_2$.

These salts are prepared by boiling phosphorus in an alkaline solution—

(α.) $3HKO + P_4 + 3H_2O = 3(KH_2PO_2) + H_3P$;

(β.) $3BaO + 2P_4 + 9H_2O = 3(Ba2H_2PO_2) + 2H_3P$.

The hypophosphites are used in medicine, as *e.g.*, *Calcis hypophosphis* B.P. (Prep.: by boiling together lime, phosphorus, and water), and *Sodæ hypophosphis*, B.P. They are commonly used in the form of syrups.

Phosphorous Anhydride, P_2O_3 (P_2O_3.)

Synonyms.—*Phosphorus Trioxide ; Phosphorus Oxide.*

Preparation.—(1.) By the slow combustion of phosphorus in dry air or in oxygen.

(2.) By burning phosphorus in a very limited supply of air.

Properties.—A white, flaky, non-crystalline, inflammable solid, very volatile, emitting a garlic-like odor. It is highly deliquescent, heat being evolved at the moment of its combination with water, and phosphorous acid formed. Phosphorous acid cannot be changed back to phosphorous anhydride by heat. If phosphorous anhydride be heated in a sealed tube, phosphoric acid and free phosphorus are formed ($5P_2O_3 = 3P_2O_5 + P_4$.)

Phosphorous Acid, H_3PO_3($POHHo_2$).

Synonym.—*Hydric Phosphite.*

Preparation. (1.) By passing moist air over phosphorus.

(2.) By the action of chlorine on melted phosphorus in hot water,

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a phosphorous chloride being first formed, which is afterwards decomposed by the water. Thus—

(α) $P_2 + 3Cl_2 = 2PCl_3$.
Phosphorus + Chlorine = Phosphorous chloride.
[$P_2 + 3Cl_2 = 2\mathbf{P}Cl_3$].

(β.) $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$.
Phosphorous chloride + Water = Phosphorous acid + Hydrochloric acid.
[$\mathbf{P}Cl_3 + 3\mathbf{O}H_2 = \mathbf{P}OHHo_2 + 3HCl$].

(3.) By the action on phosphorus of a saturated solution of cupric sulphate, whereby an insoluble copper phosphide is formed, phosphorous and sulphuric acids remaining in solution. The latter is to be precipitated by baryta water.

(4.) By heating phosphorous chloride with crystallized oxalic acid.

Properties. (a.) *Sensible and Physical.*—A thick syrupy liquid, from which deliquescent crystals may be obtained. It is decomposed by heat into phosphoric acid and phosphoretted hydrogen ($4H_3PO_3 = 3H_3PO_4 + PH_3$).

(β.) *Chemical.*—When phosphorous acid is exposed to the air phosphoric acid is formed. By the action of phosphorous acid on the salts of mercury, silver, gold, etc., the metal is reduced. With mercuric chloride it first precipitates calomel. It reduces sulphurous acid, free sulphur being deposited by the secondary action of the H_2S on the SO_2 ($2SO_2 + 2H_2O + 6H_3PO_3 = 2H_2S + 6H_3PO_4$).

Phosphorous acid is a bibasic acid; one or two hydrogen atoms being capable of substitution by a metal. Thus—

Salts (with monads) { Acid $M'H_2PO_3$ as KH_2PO_3. Normal $M_2'HPO_3$ as K_2HPO_3.

Other Salts (with dyads) { Acid $M''(H_2PO_3)_2$. Normal $M''HPO_3$.

It is to be noted, however, that *phosphorous acid is tribasic* in the phosphorous ethers, where, as in triethyl phosphorous acid ($(C_2H_5)_3PO_3$), all three hydrogens of the acid are replaced by alcohol radicals; but it must be remembered that even here only two of the compound radicals of these compounds, can be replaced by metals.

To distinguish phosphorous from hypophosphorous acid, *see* page 132.

Phosphoric Anhydride, P_2O_5($\mathbf{P}_2O_5$).

Preparation.—By burning phosphorus in oxygen or in dry air. It *cannot* be prepared by the action of heat on hydrated phosphoric acid.

Properties.—Phosphoric anhydride is a white, flaky, deliquescent solid, fusible and volatile at a red heat, subliming unchanged, and greedy of moisture. It hisses when thrown into water, due to the rapidity of its combination with water, which cannot be again completely expelled by heat. Heated with carbon it yields carbonic oxide and phosphorus.

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Phosphoric anhydride combines with either one, two, or three molecules of water, forming three acids as follows:—

(1.) $P_2O_5+H_2O=2HPO_3$ =metaphosphoric acid.

(2.) $P_2O_5+2H_2O=H_4P_2O_7$ =pyrophosphoric acid.

(3.) $P_2O_5+3H_2O=2H_3PO_4$=ortho- or common phosphoric acid.

We must consider these in order.

Metaphosphoric Acid ($HPO_3=80$) ($\mathbf{P}O_2Ho$).

Synonyms.—*Hydric Metaphosphate; Monohydrogen Phosphate* (Roscoe).

Preparation.—(1.) By dissolving phosphoric anhydride in water ($P_2O_5+H_2O=2HPO_3$).

(2.) By the action of heat on orthophosphoric acid, whereby glacial metaphosphoric acid is formed.

Properties.—A colorless solid, very soluble in water. The acid in solution changes to orthophosphoric acid slowly at ordinary temperatures, but rapidly when boiled.

The metaphosphates are formed by the action of heat either on a *dihydric phosphate* of a fixed base ($NaH_2PO_4=NaPO_3+H_2O$), or on a *monohydric phosphate* containing one atom of a volatile base ($NH_4NaHPO_4=NH_3+H_2O+NaPO_3$), or on a *dihydric pyrophosphate* ($Na_2H_2P_2O_7=H_2O+2NaPO_3$).

Tests.—(1.) *Argentic nitrate*, a white precipitate ($AgPO_3$).

(2.) The acid coagulates albumen.

Pyrophosphoric Acid ($H_4P_2O_7=178$). ($\mathbf{P}_2O_3Ho_4$).

Synonym.—*Tetrahydric Pyrophosphate; Hydrogen Pyrophosphate* (Roscoe).

Preparation.—(1.) By heating orthophosphoric acid to 419° F. (215° C.)

(2.) By decomposing plumbic pyrophosphate ($Pb_2P_2O_7$) with sulphuretted hydrogen:—

$$Pb_2P_2O_7 + 2H_2S = 2PbS + H_4P_2O_7.$$

Plumbic pyrophosphate + Sulphuretted hydrogen = Plumbic sulphide + Pyrophosphoric acid.

$$[\mathbf{P}_2O_3Pbo''_2 + 2\mathbf{S}H_2 = 2\mathbf{Pb}S'' + \mathbf{P}_2O_3Ho_4].$$

Plumbic pyrophosphate may be prepared thus. If the rhombic crystals of common sodic phosphate ($Na_2HPO_4+12H_2O$) be heated, it first becomes anhydrous sodic phosphate (Na_2HPO_4), and afterwards by further heat sodic pyrophosphate ($Na_4P_2O_7$), the crystals of which are acicular. This change results from a combination of two molecules of Na_2HPO_4, and the expulsion therefrom of one molecule of water.

$$\left.\begin{matrix}Na_2HPO_4\\Na_2HPO_4\end{matrix}\right\} = Na_4P_2O_7 + H_2O.$$

Common sodic phosphate = Sodic pyrophosphate + Water.

$$2\mathbf{P}OHoNao_2 = \mathbf{P}_2O_3Nao_4 + \mathbf{O}H_2.$$

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If this sodic pyrophosphate be now dissolved in water, and plumbic acetate added, a plumbic pyrophosphate will be precipitated [$Pb_2P_2O_7$ or $\mathbf{P}_2O_3Pbo''_2$].

Properties.—Pyrophosphoric acid deposits crystals, when the solution is evaporated 'in vacuo' over sulphuric acid.

It is a tetrabasic acid. Thus with sodium, we may have all the hydrogens substituted by the metal.

Tests.—*Calcic or baric salts;* a white precipitate.

Argentic Nitrate, a white precipitate ($Ag_4P_2O_7$). If the original solution be neutral, it will remain neutral after the nitrate of silver has been added, no free acid being liberated.

Orthophosphoric Acid (H_3PO_4, or $_3H_2OP_2O_5$=98) ($\mathbf{P}OHo_3$).

Synomyms.—*Tribasic phosphoric acid; Phosphoric acid; Common phosphoric acid; Trihydric phosphate* or *Hydric phosphate.*

Natural History.—(α.) In the *animal* kingdom, orthophosphoric acid is found largely in bones, and in *guano,* which is the partially decomposed excrement of sea fowl, and in all parts of the animal as well as in all excretions and secretions. (β.) In *vegetables* it is an essential principle, "superphosphate" constituting one of their most valuable foods. (γ.) In the *mineral* kingdom it is found as phosphorite, apatite, coprolite (so named with the notion that it was petrified dung), etc. In all cases, however, it is found in combination, and chiefly with lime and magnesia.

Preparation.—(1.) By dissolving phosphoric anhydride (P_2O_5) in water, and boiling the solution.

(2.) By boiling meta- or pyro-phosphoric acids in water.

(3.) By boiling phosphorus with dilute nitric acid, the lower nitrogen oxides being evolved. (This is the method of preparing acid phosphoricum dilutum, B.P., Sp. Gr. 1·08=10 per cent. of P_2O_5).

(4.) By decomposing bone-ash ($Ca_3P_2O_8$) with strong sulphuric acid, removing the insoluble calcic sulphate, decomposing the residual acid calcic phosphate with carbonate of ammonia, filtering to separate the calcic carbonate, evaporating to dryness, igniting to get rid of ammonia and water, redissolving the residue, and boiling.

(5.) By the combustion of phosphoretted hydrogen in air or oxygen ($PH_3+2O_2=H_3PO_4$).

(6.) By decomposing the triplumbic phosphate with sulphuretted hydrogen ($Pb_32PO_4+3H_2S=2H_3PO_4+3PbS$.)

Properties.—Tribasic or common phosphoric acid is a syrupy and very acid liquid. By evaporation "in vacuo" it may be obtained in crystals. By a heat of 329° to 410° F. (160° to 210° C.), it loses water and forms *pyro*phosphoric acid ($2H_3PO_4 = H_4P_2O_7 + H_2O$), which, at a red heat, becomes glacial *meta*phosphoric ($H_4P_2O_7=H_2O+2HPO_3$).

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Orthophosphoric acid is the common phosphoric acid of common phosphates.

Orthophosphoric acid is tribasic, and forms three classes of salts by the substitution of 1, 2, or 3 hydrogens by a metal. Thus,

	With monads.	With dyads.	Examples.
1. Acid Salts ..	$M'H_2PO_4$	$M''2H_2PO_4$	$Na'H_2PO_4$ Dihydric sodic phosphate (superphosphates).
	$M'_2H.PO_4$	M''_22HPO_4	Na'_2HPO_4 Common sodic phosphate.
2. Neutral Salts ..	M'_3PO_4	M''_32PO_4	Na'_3PO_4 Trisodic phosphate.

When these salts are heated, they lose water and form other salts. Further, the base need not be necessarily confined to one metal; thus, in microcosmic salt (the sodic-ammonic hydric phosphate) for example, we have three different basyls in one compound. Thus—

$$NaH_4NHPO_4,4H_2O$$

$$[\mathbf{P}ONaoNH_4oHo,4\mathbf{O}H_2.]$$

Tests.—*Reactions of ortho- or common phosphoric acid.*

(*a.*) *In a free or combined state in an acid solution.*

(1.) *Ammonic molybdate*, a yellow precipitate, when heated, of ammonic molybdophosphate, soluble in ammonia.

(*b.*) *In a combined state.*

(1.) *Lime* or *baryta water*, a white precipitate.

(2.) *Ammonia* and *magnesic sulphate*, a white precipitate :— ($Mg''H_4NPO_46H_2O$ or $\mathbf{P}OAmoMgo'',6\mathbf{O}H_2$), insoluble in ammonia, soluble in acids. This ignited becomes $Mg_2P_2O_7$.

(3.) *Argentic nitrate*, a yellow precipitate (Ag_3PO_4), the solution, although previously neutral, becoming acid. Soluble in ammonia and in nitric acid.

(4.) *Plumbic acetate* or *mercurous* or *bismuth nitrate*, white precipitates (Pb_32PO_4).

(5.) Whitish yellow precipitates, with *uranic nitrate* or *ferric chloride*, soluble in ammonia and in hydrochloric acid.

Uses.—*In nature* it plays an important part in animal and vegetable tissues.

In the arts it is used in calico printing, and *in medicine* its use is indicated in such diseases as rickets, etc.

[*Ammoniæ phosphas* (NH_4) $2HPO_4$ is made by adding ammonia to phosphoric acid, and allowing the crystals to form. *Calcis phosphas* (Ca_32PO_4) prepared from bones (os ustum, B.P.) as already described. *Sodæ phosphas* ($Na_2HPO_4,12H_2O$), prepared from the acid phosphate of calcium, by the addition of sodic carbonate ($Ca2H_2PO_4+Na_2CO_3 = Na_2HPO_4+H_2O+CO_2+CaHPO_4$). *Ferri phosphas* ($Fe_32PO_4$) prepared by adding sodic phosphate and acetate to ferrous sulphate ($3FeSO_4+2Na_2HPO_4+2NaC_2H_3O_2 = Fe_32PO_4+3Na_2SO_4+2C_2H_4O_2$).

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Acidum phosphoricum dilutum, prepared by the action of nitric acid on phosphorus.]

GENERAL REMARKS ON THE ACIDS OF THE OXIDES OF PHOSPHORUS.

It will be convenient here to generalise on the acids of the oxides of phosphorus.

1. There are three modifications of phosphoric acid known, viz. :—

(*a*.) Meta- or monohydric or monobasic phosphoric acid—HPO_3, or H_2O,P_2O_5.

(*β*.) Pyro- or tetrahydric or tetrabasic phosphoric acid—$H_4P_2O_7$, or $2H_2O,P_2O_5$.

(*γ*.) Ortho- or trihydric or tribasic phosphoric acid—H_3PO_4, or $3H_2O,P_2O_5$.

2. These acids may be severally prepared by passing sulphuretted hydrogen through water containing, in suspension, the corresponding silver or lead salt. Thus,

(*a*.)	$2AgPO_3$	+ H_2S	=	$2HPO_3$	+	Ag_2S.
	Argentic meta-phosphate	+ Sulphuretted hydrogen	=	Metaphosphoric acid	+	Argentic sulphide.
	[$2PO_2Ago$	+ SH_2	=	$2PO_2Ho$	+	SAg_2].
(*β*.)	$Ag_4P_2O_7$	+ $2H_2S$	=	$H_4P_2O_7$	+	$2Ag_2S$.
	Argentic pyro-phosphate	+ Sulphuretted hydrogen	=	Pyrophosphoric acid	+	Argentic sulphide.
	[$P_2O_3Ago_4$	+ $2SH_2$	=	$P_2O_3Ho_4$	+	$2SAg_2$].
(*γ*.)	$2Ag_3PO_4$	+ $3H_2S$	=	$2H_3PO_4$	+	$3Ag_2S$.
	Argentic Ortho-phosphate	+ Sulphuretted hydrogen	=	Orthophosphoric acid	+	Argentic sulphide.
	[$2POAgo_3$	+ $3SH_2$	=	$2POHo_3$	+	$3SAg_2$].

3. (*a*.) The solution of P_2O_5 in cold water forms:—

Metaphosphoric acid, H_2O,P_2O_5 or PO_2Ho.

(*β*.) This solution (other hydrates being present) on boiling becomes :—

Pyrophosphoric acid, $2H_2O,P_2O_5$ or $P_2O_3Ho_4$.

(*γ*.) Whilst on prolonged boiling it yields:—

Orthophosphoric acid, $3H_2O,P_2O_5$ or $POHo_3$.

4. These acids are distinguished from one another by their reactions on albumen, on argentic nitrate, and on baric nitrate as follows :—

	On Albumen.	On Argentic nitrate.	On Baric nitrate.
(*a*.) Metaphospho-ric acid	Coagulates	White gelatinous ppt. ($AgPO_3$).	White ppt.
(*β*.) Pyrophospho-ric acid	No action	No ppt. unless rendered alkaline, when it gives a *white* ppt. ($Ag_4P_2O_7$).	No ppt. unless alkaline, when it gives a white ppt.
(*γ*.) Orthophospho-ric acid	No action	No ppt. unless rendered alkaline, when it gives a *yellow* ppt. (Ag_3PO_4).	Ditto ditto.

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5. These acids form corresponding salts as follows :—

(α.) *Metaphosphates*, or monophosphates—

$M'PO_3$ { $Na'PO_3$ ($\mathbf{P}O_2Nao$). / $Pb''2PO_3$ ($\mathbf{P}_2O_4Pbo''$).

(β.) *Pyrophosphates*, or tetraphosphates—

$M'_4P_2O_7$ { $Na'_4P_2O_7 + 10H_2O$ ($\mathbf{P}_2O_3Nao_4, 10\mathbf{O}H_2$). / $Pb''_2P_2O_7$ ($\mathbf{P}_2O_3Pbo''_2$).

(γ.) *Orthophosphates*, or triphosphates—

M'_3PO_4 {
NaH_2PO_4, H_2O ($\mathbf{P}OHo_2Nao, \mathbf{O}H_2$).
$Na_2HPO_4, 12H_2O$ ($\mathbf{P}OHoNao_2, 12\mathbf{O}H_2$).
$Na_3PO_4, 12H_2O$ ($\mathbf{P}ONao_3, 12\mathbf{O}H_2$).
$Na, H_4N, HPO_4, 4H_2O$ ($\mathbf{P}O, Ho, NaoAmo4\mathbf{O}H_2$).
$Ca''_3 2PO_4$ ($\mathbf{P}_2O_2Cao''_3$).
$Ca'', H_4 2PO_4$ ($\mathbf{P}_2O_2Ho_4Cao''$).

6. All forms of phosphates may be converted into tribasic phosphates by fusion with an alkaline hydrate, or carbonate.

7. It will be further noted that if water or ammonia (these being volatile) enter into the composition of the salts, heat will convert an orthophosphate into a pyrophosphate, and a pyrophosphate into a metaphosphate. This will be better seen as follows :—

(1.) *Disodic hydric orthophosphate* $(Na_2O)_2H_2O,P_2O_5$ when heated, becomes *Sodic pyrophosphate.* $(Na_2O)_2,P_2O_5$.

(2.) *Sodic hydric pyrophosphate* Na_2O,H_2O,P_2O_5 „ „ *Sodic metaphosphate.* Na_2O,P_2O_5.

(3.) *Sodic ammonic hydric orthophosphate* $Na_2O,(NH_4)_2O,H_2O,P_2O_5$ (Microcosmic salt) „ „ *Sodic metaphosphate.* Na_2O,P_2O_5.

(8.) The reaction of the several salts after the addition of argentic nitrate is important.

(α.) A solution of metaphosphate of soda (Na_2O,P_2O_5 or $NaPO_3$) is slightly *acid.* On adding argentic nitrate, *a white gelatinous precipitate* is thrown down, and the solution becomes *neutral,* thus—

$NaPO_3 + AgNO_3 = AgPO_3 + NaNO_3$.

Sodic metaphosphate + Argentic nitrate = Argentic metaphosphate + Sodic nitrate.

$\mathbf{P}O_2Nao + \mathbf{N}O_2Ago = \mathbf{P}O_2Ago + \mathbf{N}O_2Nao$.

(β.) A solution of sodic pyrophosphate ($2Na_2O,P_2O_5$, or $Na_4P_2O_7$) is *alkaline.* On adding argentic nitrate *a white precipitate* is thrown down, and the solution becomes *neutral.* Thus—

$Na_4P_2O_7 + 4AgNO_3 = Ag_4P_2O_7 + 4NaNO_3$.

Sodic pyrophosphate + Argentic nitrate = Argentic pyrophosphate + Sodic nitrate.

$\mathbf{P}_2O_3Nao_4 + 4\mathbf{N}O_2Ago = \mathbf{P}_2O_3Ago_4 + 4\mathbf{N}O_2Nao$.

(γ.) A solution of sodic orthophosphate ($NaO,2H_2O,P_2O_5$ or Na_2HPO_4) is *alkaline.* On adding argentic nitrate *a yellow precipitate* is thrown down, and the solution becomes *acid.* Thus—

$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3$.

Sodic orthophosphate + Argentic nitrate = Argentic orthophosphate + Sodic nitrate + Nitric acid.

$\mathbf{P}OHoNao_2 + 3\mathbf{N}O_2Ago = \mathbf{P}OAgo_3 + 2\mathbf{N}O_2Nao + \mathbf{N}O_2Ho$.

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(9.) Other varieties of phosphates have been described by Fleitmann and Henneberg:—

(α.) By heating together one molecule of sodic pyrophosphate and two of metaphosphate, a salt is obtained consisting of $2Na_3PO_4,P_2O_5$.

(β.) By heating one molecule of pyrophosphate with eight of metaphosphate, a salt is obtained consisting of $4Na_3PO_4,3P_2O_5$. Corresponding silver and magnesium compounds have been obtained.

These compounds are very unstable, quickly becoming a mixture of pyrophosphate and metaphosphate. It would thus seem that the following phosphates have been prepared, viz.:—

Orthophosphates	$6M_2O,2P_2O_5$ or $4M_3PO_4$.
Pyrophosphates	$6M_2O,3P_2O_5$ or $3M_4P_2O_7$.
Fleitmann and Henneberg's salt (α)	$6M_2O,4P_2O_5$ or $2M_6P_4O_{13}$.
Do. do. (β)	$6M_2O,5P_2O_5$ or $M_{12}P_{10}O_{31}$.
Metaphosphates	$6M_2O,6P_2O_5$ or $12MPO_3$.

Compounds of Phosphorus and the Haloids, etc.

With Chlorine.	With Bromine.	With Iodine.
Trichloride .. PCl_3	Tribromide .. PBr_3	Diiodide .. .. PI_2
Pentachloride .. PCl_5	Pentabromide .. PBr_5	Triiodide .. .. PI_3
Oxytrichloride .. $POCl_3$	Oxytribromide .. $POBr_3$	
Sulphotrichloride $PSCl_3$	Sulphotribromide $PSBr_3$	

Phosphorous Chloride, PCl_3($\mathbf{P}Cl_3$).

Molecular weight, 137·5. *Relative weight*, 68·75. *Molecular volume*, □|□. *Specific gravity of liquid*, 1·516; *of vapor*, 4·79.

Synonyms.—*Trichloride or Terchloride of Phosphorus.*

Preparation. (1.) By passing phosphorus vapor over heated mercuric chloride (corrosive sublimate).

(2.) By the action of chlorine on dry melted phosphorus ($P_2+3Cl_2 = 2PCl_3$).

Properties.—A transparent colorless volatile liquid, soluble in benzol and in carbonic disulphide. It dissolves phosphorus and also absorbs chlorine freely, forming PCl_5. At its boiling point, 165·2° F., (74° C.) it absorbs oxygen, forming $POCl_3$. It is decomposed by alcohol, by ether, and by a large excess of water, in the latter case hydrochloric and phosphorous acids being produced. If hot water be used the re-action is very violent.

PCl_3	+	$3H_2O$	=	$3HCl$	+	H_2PHO_3.
Phosphorous chloride	+	Water	=	Hydrochloric acid	+	Phosphorous acid.
[$\mathbf{P}Cl_3$	+	$3\mathbf{O}H_2$	=	$3HCl$	+	$\mathbf{P}OHHo_2$.]

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Phosphoric Chloride, PCl_5($\mathbf{P}Cl_5$).

Molecular weight, 208·5. *Molecular volume*, *to* .

Relative weight, 52·1 *to* 104·25. *Specific gravity of vapor at* 572° F. (300° C.) 3·654.

Synonyms.—*Pentachloride or Perchloride of Phosphorus.*

Preparation.—(1.) By the action of chlorine either on dry phosphorus in an exhausted flask, or on phosphorous chloride ($PCl_3+Cl_2=PCl_5$).

(2.) By passing chlorine through a solution, artificially cooled, of phosphorus in carbonic disulphide. The solution is afterwards evaporated to dryness.

Properties.—A white deliquescent crystalline solid, volatile (before melting) at 212° F. (100° C.) It may be fused under pressure at 298° F. (148° C.) It burns when passed into a flame, chlorine and phosphoric anhydride being formed. It combines with ammonia. When acted on with acids or with alcohols it forms chlorides of the radicals of the said alcohols and acids. Thus—

C_2H_6O or $\begin{cases}\mathbf{C}H_3\\ \mathbf{C}H_2Ho\end{cases}$	becomes	C_2H_5Cl or $\begin{cases}\mathbf{C}H_3.\\ \mathbf{C}H_2Cl.\end{cases}$
Ethylic Alcohol	becomes	*Ethylic Chloride.*

It is decomposed by an excess of water, hydrochloric and phosphoric acids being formed:—

PCl_5	+	$4H_2O$	=	$5HCl$	+	H_3PO_4.
Phosphoric chloride	+	Water	=	Hydrochloric acid	+	Phosphoric acid.
[$\mathbf{P}Cl_5$	+	$4\mathbf{O}H_2$	=	$5HCl$	+	$\mathbf{P}OHo_3$].

Phosphoric Oxytrichloride, $POCl_3$($\mathbf{P}OCl_3$).

Molecular weight, 153·5. *Molecular volume*, . *Relative weight*, 76·75. *Specific gravity of liquid*, 1·7; *of vapour*, 5·298. *Boils at* 230° F. (110° C.).

Synonyms.—*Phosphoryl Chloride or Trichloride; Oxychloride of Phosphorus.*

Preparation. (1.) By the slow action of a small quantity of water on phosphoric chloride ($PCl_5+H_2O=POCl_3+2HCl$).

(2.) By passing oxygen through boiling phosphorous chloride ($PCl_3+O=POCl_3$).

(3.) By heating together phosphoric chloride and phosphoric anhydride ($3PCl_5+P_2O_5=5POCl_3$).

(4.) By heating an acid (such as oxalic or boracic acid) with phosphoric chloride (Gerhardt) ($5PCl_5 + 2(BH_3O_3) = 3POCl_3 + 6HCl + B_2O_3$).

Properties.—A volatile limpid fuming liquid, decomposed by water

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into hydrochloric and phosphoric acids ($POCl_3 + 3H_2O = H_3PO_4 + 3HCl$).

The importance of this compound, as well as of the other chlorides of phosphorus, depends on its action in producing various organic substitution products.

The bromides and oxybromide of phosphorus correspond to the chlorine compounds.

Phosphoric Sulphotrichloride, $PSCl_3$ ($PS''Cl_3$).

Molecular weight, 169·5. *Specific gravity of liquid*, 1·631; *of vapor*, 5·878. *Boils at* 257° F. (125° C.).

Synonyms.—*Sulphochloride of Phosphorus.*

Preparation.—(1.) By decomposing phosphoric chloride with sulphuretted hydrogen ($PCl_5 + SH_2 = PSCl_3 + 2HCl$).

(2.) By decomposing phosphoric chloride with antimonious sulphide ($3PCl_5 + Sb_2S_3 = 3PSCl_3 + 2SbCl_3$).

Properties.—A colorless, fuming liquid. When boiled with sodic hydrate, it forms sodic chloride and trisodic sulphophosphate; from this latter the corresponding barium, calcium, and strontium salts may be prepared by double decomposition. (Wurtz.)

$6NaHO$	+	$PSCl_3$	=	$3NaCl$	+	Na_3PSO_3	+	$3H_2O$.
Sodic hydrate	+	Phosphoric sulphotrichloride	=	Sodic chloride	+	Trisodic sulphophosphate	+	Water.
$[6ONaH$	+	$PSCl_3$	=	$3NaCl$	+	$PS''Nao_3$	+	$3OH_2$.

It is decomposed by water forming phosphoric, hydrochloric, and hydrosulphuric acids ($2PSCl_3 + 8H_2O = 2H_3PO_4 + 6HCl + 2H_2S$.)

The Iodides of Phosphorus.

The Di- or Biniodide of Phosphorus (PI_2) is prepared by adding 2 atoms of iodine to 1 atom of phosphorus dissolved in carbonic disulphide, and subsequently cooling the mixture. It forms orange-coloured prismatic crystals, melting at 230° F. (110° C.), and decomposed by water. It has no analogue amongst oxygen, chlorine, or bromine compounds.

The **Triiodide** (PI_3) is prepared similarly to the diiodide by using proper atomic proportions of the constituents. It forms dark red deliquescent six-sided plates, melting at 130° F. (55° C.).

By heating 100 atoms of phosphorus with 1 of iodine the whole of the phosphorus may be changed into the red or Schrötter's phosphorus (*see* page 128).

Other compounds of oxygen and the halogens with phosphorus have been described, viz., *pyrophosphoryl chloride* ($P_2O_3Cl_4$), *phosphorus bromochloride* (PCl_3Br_2), *phosphoryl chlorobromide* ($POCl_2Br$), *phosphorus sulphobromochloride* ($PSCl_2Br$), etc.

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Phospham (HN_2P?).

Preparation.—By saturating phosphorous chloride (cooled by a freezing mixture) with ammonia gas, a white saline mass ($5H_3N,PCl_3$), is obtained. This is now heated in a current of CO_2 until all the sal-ammoniac is sublimed. The residue constitutes *Phospham*. (Gerhardt.)

Properties.—A yellowish-white bulky amorphous powder, termed phosphide of nitrogen by Rose. Its composition is probably HN_2P. Rose overlooked the presence of hydrogen in the body, inasmuch as phospham is unaffected by chlorine, and, provided no air be present, may be heated to redness without change.

Action of Ammonia on Phosphorus Compounds.

(1.) When *anhydrous* phosphoric acid (P_2O_5) is heated with ammonia, *phosphamic acid* ($N_2H_4P_2O_4$) is formed, ($2NH_3+P_2O_5=H_2O+N_2H_4P_2O_4$). When phosphamic acid is heated with water it forms the acid phosphate of ammonia ($N_2H_4P_2O_4+4H_2O=(NH_4)_2O.2H_2O.P_2O_5$).

The *phosphamate of ammonia*, heated in a current of dry ammonia loses water, and becomes *phospham*. Thus :—

$(NH_4)_2ON_2H_4P_2O_4$	=	$5H_2O$	+	$2HN_2P$.
Phosphamate of Ammonia	=	Water	+	Phospham.

(2.) When *phosphoric chloride* (PCl_5) is heated with ammonia, *chloro-phosphamide* ($N_2H_4PCl_3$) is formed, ($PCl_5+2NH_3=2HCl+N_2H_4PCl_3$). By boiling this body with water it becomes *phosphodiamide* (N_2H_3PO); ($N_2H_4PCl_3+H_2O=N_2H_3PO+3HCl$) which by heating becomes *mono-phosphamide* (NPO); ($N_2H_3PO=NH_3+NPO$).

(3.) By the action of ammonia on *oxychloride of phosphorus* ($POCl_3$) *phosphotriamide* is formed (N_3H_6PO).

(4.) By the action of ammonia on *sulphochloride of phosphorus* ($PSCl_3$) *sulphosphotriamide* is formed (N_3H_6PS).

These *amides* are derivatives of ammonia salts by the loss of water molecules.

$(NH_4)_2O,2H_2O,P_2O_5 - 6H_2O = 2NPO$, Monophosphamide.
$2(NH_4)_2O,H_2O,P_2O_5 - 6H_2O = 2N_2H_3PO$, Phosphodiamide.
$3(NH_4)_2O,P_2O_5 - 6H_2O = 2N_3H_6PO$, Phosphotriamide.
$(NH_4)_2O,2H_2O,P_2O_5 - 4H_2O = N_2H_4P_2O_4$, Phosphamic acid.

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CHAPTER VII.

SULPHUR—SELENIUM—TELLURIUM.

SULPHUR.—Compounds of Sulphur with Oxygen and Hydroxyl—Sulphurous anhydride and acid — Sulphuric anhydride and acid — Hyposulphurous acid — Thiosulphuric acid — Dithionic acid — Trithionic acid — Tetrathionic acid — Pentathionic acid — Compounds of Sulphur and Chlorine — Compounds of Sulphur, Oxygen and the Haloids—Compounds of Sulphur and Phosphorus. SELENIUM.—Compounds of Selenium and Oxygen. TELLURIUM.—Compounds of Tellurium and Oxygen.

SULPHUR (S_2).

Atomic weight, 32. *Molecular weight*, 64. *Molecular volume at* 1000° C. $\boxed{\ |\ |\ }$, *below this, one-third. Atomicity, Hexad* ($S^{vi}O_2Ho_2$), *Tetrad* ($S^{iv}O_2$), *Dyad* ($S''H_2$). *Relative weight*, 32. *Specific gravity of solids, various; of vapor, at* 900° F. (482·2° C.), 6·617, *and at* 1904° F. (1040° C.), 2·23; *melts at* 239° F. (115° C.); *boils at* 836° F. (446° C.).

Synonyms.—*Pyrites* ($\pi\nu\rho$ fire); *Brimstone* (*Brume* or *Breinse* fire, and *Stein* a stone); *Sulphur* (*sal* salt, and $\pi\nu\rho$ fire.)

History.—Sulphur was known in early times. It is mentioned by Moses, Homer, and Pliny, and is referred to by Geber as one of the principles of nature. It was considered by the alchemists to constitute the impurity of the baser metals. In the middle ages it was regarded as the principle of fire, and every combustible body was supposed to contain it.

Natural History.—(α.) In the *mineral* kingdom sulphur is found (1) in a *free* state in many volcanic districts, either in yellow crystals or in opaque amorphous masses embedded in blue clay and in fissures in gypsum and celestine (virgin or native sulphur). [When sulphuretted hydrogen, steam, and air are passed over calcic carbonate at 212° F. (100° C.) gypsum is formed, and sulphur deposited.] (2.) It is found in combination with hydrogen, in certain mineral waters (Harrogate), and with the metals, as *sulphides* (FeS_2, *iron pyrites;* $Cu_2S.Fe_2S_3$, *copper pyrites;* PbS, *galena;* ZnS, *blende;* Sb_2S_3, *crude antimony;* HgS, *cinnabar*). (3.) It is also found as *sulphates*, as *e.g.*, sulphates of *lime* (gypsum, $CaSO_4$), *baryta* (heavy spa, $BaSO_4$), *strontia* (celestine; $SrSO_4$), *magnesia* (Epsom salts, $MgSO_4$), and *soda* (Glauber salts, Na_2SO_4).

(β.) In the *vegetable* kingdom it is present in albumen, gluten, etc., and also in the acrid volatile oils, such as essence of mustard (C_4H_5NS); whilst (γ.) in the *animal kingdom* it is found as a constituent of albumen, fibrin, and casein, in muscular tissue, hair, bile, etc.

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Preparation.—(1.) By a rude process of simply melting out the sulphur from its impurities.

(2.) By distilling the sulphur in earthenware retorts, and allowing the distillate to flow into water. This "rough sulphur," as it is called, is redistilled in iron retorts, and the sulphur collected either in cooled brickwork chambers (forming flowers of sulphur), or else as a liquid which is afterwards cast into rolls (forming roll sulphur.)

(3.) *By the distillation of iron or copper pyrites.*—The pyrites is heated either (α) *in close vessels*, when one-third of the sulphur is driven off, and magnetic pyrites remain ($3FeS_2 = Fe_3S_4 + S_2$), or (β) *in the open air.* This is done in the case of copper pyrites as a preliminary stage to copper roasting. The pyrites heaped on brushwood and fired from a central flue, is kept burning for months, and the sulphur therefrom collected in pits. The sulphur prepared from pyrites generally contains a little arsenic.

(4.) By distilling the spent oxide of iron used in gas purification. The oxide, by successive revivifications,* becomes charged with from 40 to 60 per cent. of sulphur ($\underbrace{2FeS + H_2O}_{\text{Spent oxide.}} + O_3 = Fe_2O_3 + OH_2 + S_2$).

(5.) It is also prepared from the tank waste of alkali works.

Varieties.—(1.) *Native sulphur.*—This variety occurs naturally, and may also be obtained by the spontaneous evaporation of a solution of sulphur in carbonic disulphide. It consists of transparent yellow crystals (octahedra), which are unaltered by exposure to air. It has a specific gravity of 2·05. It fuses at 239° F. (115° C.) It is the most stable of the sulphur allotropes, and is the ultimate condition which all the other varieties assume.

(2.) *Yellow sulphur.*—This may be crystallised by fusion (oblique prisms). It is brownish yellow when first prepared, but changes by exposure to air to an opaque yellow. This alteration is attended with a change of form (octahedra) and the evolution of heat. It has a specific gravity of 1·98. It fuses at 248° F. (120° C.).

(3.) *Ductile sulphur.*—This is prepared by pouring melted sulphur (800° F.) into cold water. By exposure to air it changes into the crystalline variety, becoming yellow and brittle, evolving heat during the alteration. A similar change may be effected by heating the ductile sulphur to 230° F. (110° C.).

(4.) *A Buff Amorphous Variety.*—This constitutes the insoluble residue that remains after exhausting the flowers of sulphur, or the ductile variety after prolonged exposure to air, with carbonic disulphide.

(5.) *White Variety* (milk of sulphur).—This is prepared by precipitating a solution of sulphur in an alkali (an alkaline polysulphide) with an acid:—

$$(K_2S_5 + 2HCl = 2KCl + H_2S + 2S_2).$$

* By revivification the moist ferrous sulphide is changed into ferric hydrate and sulphur.

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A Black Variety has also been described by Magnus, as well as one of a *red* color, but of these our knowledge is not complete.

These allotropic forms of sulphur may be thus classified :—

	1. Octahedral.	2. Prismatic.	3. Ductile.	4. Amorphous powder.	5. White amorphous variety.
Color	Transparent yellow.	Brownish yellow.	Deep amber.	Buff.	White.
Form	Crystals—Octahedra with rhombic base.	Oblique prisms.	Plastic amorphous mass.	Amorphous powder.	Amorphous powder.
Specific grav.	2·05.	1·98.	1·95.	1·95.	
Melting point	239° F. (115° C.)	248° F. (120° C.)			
Action of carbonic disulphide . .	Soluble.	Soluble (changed into form No. 1).	Not soluble.	Not soluble.	Very soluble.

Properties.—The properties of sulphur differ according to the variety :

(*α.*) *Sensible and Physiological.*—Sulphur is met with in commerce, either as roll sulphur or as flowers of sulphur. It crystallizes in two distinct forms, viz., in octahedra and in oblique prisms (dimorphous). Ordinary sulphur is yellow, but the colors of its allotropes are various. Native sulphur is transparent, but all the other forms are opaque. It has no taste or smell. Its medicinal action is mildly laxative.

(*β.*) *Physical.—The specific gravity* of the *transparent crystalline* variety is 2·05 ; of the *prismatic* 1·98 ; of the *ductile* and the *amorphous powder* 1·95. The specific gravity of the vapor at 900° F. (482·2° C.) is 6·617, whilst at 1904° F. (1040° C.) it is 2·222. (Deville.) Thus, at 1904° F. sulphur vapor becomes dilated to three times the bulk it occupies at 900° F. This fact is important. We mean by specific gravity the weight of a body compared with an equal volume of dry air at the same temperature and pressure. Hence the actual temperature, in the case of most gases and vapors, is of no consequence. For example, whether oxygen be compared to air at 60° F., or to air at 600° F., so long as both oxygen and air be at the same temperature when the comparison is made, their weights relatively would be as 1·1057 to 1·000. In the case of sulphur vapor, however, its specific gravity at 900° F. is 6·617 ; that is, it is six and a-half times heavier than air at 900° F., the atom being, therefore, 96 times as heavy as hydrogen. It follows, therefore, that the atomic weight of sulphur being 32, the atom would only occupy $\frac{1}{3}$ of a volume. But at 1904° F. its specific gravity becomes 2·222 ; that is, the sulphur vapor is about two and a-quarter times as heavy as air at 1904° F. It is evident, therefore, that sulphur vapor is only a true gas at this higher temperature, one atom of sulphur occupying one volume, and being 32 times the weight of a hydrogen atom.

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Action of Heat.—Sulphur is a bad conductor of heat. When held in the hand it crackles, owing to unequal expansion. It is slightly volatile at common temperatures, and freely volatile at 280° F. (137·8° C.). The octahedral variety fires at 239° F. (115° C.), and the prismatic at 248° F. (120° C.). It boils at 836° F. (446·6° C.). The action of heat on sulphur is remarkable, and may be examined under the heads of Fluidity, Color and Form.

(1.) *In respect of Fluidity.*—At a temperature of from 250° to 280° F. (121° to 138° C.) sulphur becomes liquid; at 350° F. (170° C.) it becomes thick and viscid; and at 500° F. (260° C.) it again becomes liquid.

(2.) *In respect of Color.*—The sulphur remains yellow to 280° F. (137·8° C.). At from 280° F. to 350° F. (138° to 177° C.) it becomes orange; at from 350° to 400° F. (177° to 204° C.) it turns a reddish color; at from 400° to 500° F. (204° to 260° C.) it becomes dark brown; whilst at 600° F. (316° C.) it becomes black.

(3.) *In respect of Form.*—When sulphur is heated to 239° F. (115° C.) and cooled slowly, its crystals are right prisms; when heated above this temperature and cooled slowly, it forms oblique prisms; whilst, if heated above 500° F. (260° C.), and then cooled rapidly, it assumes the elastic and amorphous modification.

We may state these facts generally as follows:—When the sulphur is heated to 280° F. (138° C.) it becomes liquid. As the heat is continued, it gradually becomes thick and viscid, until at 350° F. (176·7° C.) the liquid becomes so thick that it will not fall out of the vessel when inverted. It remains at this temperature for some time, notwithstanding the continuous application of heat. At from 350° to 500° F. its fluidity is restored, and it assumes a dull brown color. If it be now poured into cold water, the elastic variety is produced. In the change from the elastic to the common yellow modification, the heat absorbed at 350° F. (176·7° C.) is evolved. When the melted sulphur is allowed to cool, it passes through the same stages *inversely* as when heated, that is, it first becomes viscous, then fluid, and finally solid.

Sulphur is a non-conductor of electricity, becoming negatively electrical by friction. All the varieties of sulphur are insoluble in water, but are soluble in alcohol, chloroform, and ether, and (excepting the amorphous modification) in turpentine, chloride of sulphur, benzene, the fixed oils, and more particularly in carbonic disulphide.

(γ.) *Chemical.*—Sulphur is combustible at from 450° to 500° F. (235° to 260° C.) burning with a blue flame, and forming SO_2. It combines freely with all the non-metals except nitrogen, and with all the metals, many of which burn in its vapor. In its chemical relations it is closely allied to oxygen. Chemically, sulphur may be divided under two heads:—

(1.) Where it is *electro-negative*, that is, where it is separated from a compound at the positive pole of the battery, as in H_2S. This form is *soluble* in carbonic disulphide.

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(2.) Where it is *electro-positive*, that is, where it is separated at the negative pole of the battery, as in SO_2 or in S_2Cl_2. This form is *insoluble* in carbonic disulphide.

Concentrated *nitric and sulphuric acids* act on sulphur slowly, the former converting it into sulphuric acid, and the latter into sulphurous acid. It is changed into sulphuric acid by the action of nitric acid and potassic chlorate. The alkalies dissolve phosphorus when heated with it, a mixture of a hyposulphite and a sulphide of the metal being formed.

Uses.—In the *arts*, sulphur is used in match-making, in preparing vulcanised caoutchouc, in bleaching, and in the manufacture of gunpowder and oil of vitriol. In *medicine* it is used as a laxative, and in various forms of cutaneous diseases. In the preparation of the *sulphur precipitatum* (milk of sulphur), the pharmacopœia directs 5 parts of sulphur to be boiled in water with three parts of lime. Thus, a calcium hyposulphite and polysulphide are formed ($3CaH_2O_2 + 6S_2 = 2CaS_5 + CaS_2O_3 + 3H_2O$). The sulphur in the solution is now precipitated with hydrochloric acid ($2CaS_5 + CaS_2O_3 + 6HCl = 3CaCl_2 + 3H_2O + 6S_2$). The sulphurous acid set free by the action of the acid on the hyposulphite decomposes the sulphuretted hydrogen, set free by the action of the acid on the sulphide ($4H_2S + 2SO_2 = 3S_2 + 4H_2O$). "Milk of sulphur," however, is often precipitated by adding sulphuric acid instead of hydrochloric acid, and in this way becomes largely adulterated with calcic sulphate ($2CaS_5 + CaS_2O_3 + 3H_2SO_4 = 3CaSO_4 + 3H_2O + 6S_2$). This adulteration may be known by a residue of calcic sulphate being left on ignition.

Sometimes a trace of arsenic is present in the *sulphur sublimatum* B. P. (flowers of sulphur) prepared from pyrites.

Compounds of Sulphur with Oxygen and Hydroxyl.

Oxide or Anhydride.	Formula.	+Water^n	= Acids of Sulphur.	Constitutional formula for acids.	Name of acid.
			H_2SO_2	SHo_2	Hyposulphurous acid.*
Sulphurous anhydride	SO_2 or SO_2	$+H_2O$	$=H_2SO_3$	$SOHo_2$	Sulphurous acid.
Sulphuric anhydride	SO_3 or SO_3	$+H_2O$	$=H_2SO_4$	SO_2Ho_2	Sulphuric acid.
			$H_2S_2O_3$	$SS''OHo_2$	Thiosulphuric acid.
			$H_2S_2O_6$	SO_2Ho, SO_2Ho	Dithionic acid.
			$H_2S_3O_6$	SO_2Ho, S'', SO_2Ho	Trithionic acid.
			$H_2S_4O_6$	SO_2Ho, S'', S'', SO_2Ho	Tetrathionic acid.
			$H_2S_5O_6$	SO_2Ho, S'', S'', S'', SO_2Ho	Pentathionic acid.

Polythionic Acids ($\theta\epsilon\iota o\nu$ sulphur.)

* This will be considered after sulphuric acid.

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NOTE.—(1.) That the sulphur in these compounds is either hexad, tetrad, or dyad.

(2.) That only two anhydrides or oxides have been isolated (viz., SO_2 and SO_3).

Sulphurous Anhydride, $SO_2(\mathbf{S}O_2)$.

Molecular weight, 64. *Molecular volume*, $\boxed{\ |\ |\ }$. *Relative weight*, 32. *Specific gravity of gas*, 2·247; *of liquid*, 1·38. 1 *litre of the gas weighs* 2·217 *grms., and* 100 *cubic inches* 69·814 *grains.*

Synonyms.—*Sulphur Dioxide; Volatile Spirits of Sulphur; Phlogisticated Vitriolic Acid.*

History.—The irritation produced by burning sulphur is mentioned by Homer and Pliny. It is said to have caused the death of the elder Pliny (A.D. 79), in his curious enquiry into the eruption of Vesuvius. Its properties were studied by Stahl and by Priestley (1774), who determined its real nature by burning sulphur in pure oxygen.

Natural History.—It is found in the air of volcanic districts and in that of towns, in the former case issuing from volcanoes, and in the latter evolved from burning coal, or from roasting copper pyrites and other sulphur ores.

Preparation. — (1.) By burning sulphur in air or oxygen ($S+O_2=SO_2$).

(2.) By heating sulphuric acid with metals, as copper or mercury.

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$
Copper + Sulphuric acid = Cupric sulphate + Sulphurous anhydride + Water.

$$[Cu + 2\mathbf{S}O_2Ho_2 = \mathbf{S}O_2Cuo'' + \mathbf{S}O_2 + 2\mathbf{O}H_2.$$

(3.) By heating sulphuric acid with carbon or with any organic matter. The SO_2 evolved is mixed with CO_2.

$$2H_2SO_4 + C = 2SO_2 + CO_2 + 2H_2O.$$
Sulphuric acid + Carbon = Sulphurous anhydride + Carbonic anhydride + Water.

$$[2\mathbf{S}O_2Ho_2 + C = 2\mathbf{S}O_2 + \mathbf{C}O_2 + 2\mathbf{O}H_2].$$

(4.) By heating together sulphur and manganic peroxide.

$$S_2 + MnO_2 = SO_2 + MnS.$$
Sulphur + Manganic peroxide = Sulphurous anhydride + Manganous sulphide.

$$[S_2 + \mathbf{Mn}O_2 = \mathbf{S}O_2 + \mathbf{Mn}S''].$$

(5.) By heating together dehydrated ferrous sulphate and sulphur ($FeSO_4+S_2=FeS+2SO_2$).

The gas must be collected in dry bottles by displacement or over mercury.

Properties. (α.) *Sensible.*—A colorless gas having a strong brimstone odor.

(β.) *Physiological.*—It rapidly destroys life when in a concentrated form. When very dilute the irritation produced in the first instance

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rapidly passes off, the animal becoming tolerant of somewhat large quantities. One part in 10,000 parts of air is destructive to plant-life.

Proportion of SO_2 in 10,000 of air.	Physiological effects and chemical reactions.
4·34	Air irrespirable. Acts instantly on iodic acid and starch.
2·00	Air strong both to taste and smell. Acts on starch and iodic acid in 30 seconds.
0·86	Air strong to smell, and irritating. Acts on test paper in 2 minutes.
0·1	Smell perceptible. Acts on test paper after some time.

(γ.) *Physical.*—The gas has a specific gravity of 2·247; 100 cubic inches weigh 69·814 grains. It is freely soluble in water and in alcohol. By a pressure of three atmospheres at common temperatures, or by a cold of —0·4° F. (—18° C.) it becomes a transparent liquid having a specific gravity of 1·38, boiling at 14° F. (—10° C.) and solidifying at —105° F.(—76° C.) The solid thus formed is colorless and transparent, and melts at —110·2° F. (—79° C.)

Liquid sulphurous anhydride dissolves bitumen, phosphorus, sulphur, iodine, etc.

(δ.) *Chemical.*—Sulphurous anhydride first reddens and afterwards bleaches litmus. It will not support the combustion of a taper.

It is a powerful *reducing agent,* owing to its tendency to become oxidized. When a sulphurous acid solution is heated in a sealed tube to 340° F. (171° C.) it yields free sulphur and sulphuric acid, one portion of the sulphurous anhydride becoming oxidized at the expense of another portion ($3SO_2+2H_2O=2H_2SO_4+S$). It reduces nitric acid ($2HNO_3+SO_2=H_2SO_4+N_2O_4$); also iodic acid, setting free iodine, and also chromic, arsenic, and permanganic acids.

It is a powerful bleaching agent. It does not, however, destroy the coloring matter (as in the case of chlorine, the bleaching action of which is due to oxidation), but merely forms colorless compounds with the coloring matters. The color of the article bleached with SO_2, may be restored by the action of an alkali or of a stronger acid.

Action on Chlorine.—Sulphurous anhydride combines with chlorine in equal volumes under the influence of bright sunshine, to form *chlorosulphuric acid* or *chloride of sulphuryl* (SO_2Cl_2), a colorless liquid emitting very acrid irritating vapors. This body does not combine with bases. It is decomposed by water, forming *sulphuric* and hydrochloric acids.

NOTE.—*The chloride of thionyl* ($SOCl_2$) formed by the action of hypochlorous acid gas on a solution of sulphur in subchloride of sulphur, is also decomposed by water, *sulphurous* and hydrochloric acids being formed. An iodo-sulphuric acid has also been described.

Action on the Metals.—Sodium and potassium burn in sulphurous anhydride, forming a mixed oxide and sulphide. A similar result

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occurs when iron, lead, tin, or zinc are heated in the gas ($SO_2+3Zn=ZnS+2ZnO$).

When sulphurous anhydride is passed into a solution of a *metallic hydrate*, a sulphite is formed. It is to be noted that—

(*a.*) If the acid be in excess, *an acid sulphite* ($MHSO_3$) is formed $KHO+SO_2=KHSO_3$(**O**KH + SO_2=**S**OHoKo); but that—

(*β.*) If the hydrate be in excess, *a normal or neutral sulphite* (M_2SO_3) is formed, $2KHO+SO_2=K_2SO_3+H_2O$(2**O**KH + **S**O_2=**S**OKo_2 + **O**H_2).

Passed over *metallic peroxides*, sulphurous anhydride forms sulphates ($PbO_2+SO_2=PbSO_4$).

In the presence of moisture sulphurous acid decomposes *sulphuretted hydrogen*, pentathionic acid being formed ($10SO_2+10H_2S=5S_2+8H_2O+2H_2S_5O_6$ (pentathionic acid). The sulphur thrown down during this reaction is electro-positive, and insoluble in carbonic disulphide.

Sulphurous anhydride is a powerful antiseptic and disinfectant.

Sulphurous Acid (H_2SO_3 or **S**OHo_2.)

Water dissolves about 40 or 50 times its bulk of sulphurous anhydride, forming a sulphurous acid solution. This acid, when cooled below —40° F. (—40° C.), yields a crystalline hydrate (H_2SO_3, $8H_2O$), which fuses at 39·2° F. (4° C.). Sulphurous acid expels carbonic anhydride from its compounds. It is readily decomposed by heat into sulphurous anhydride and water, and freely absorbs oxygen from the air, forming sulphuric acid. In the presence of nascent hydrogen it forms sulphuretted hydrogen. It dissolves and is decomposed by those metals which evolve hydrogen with hydrochloric acid. It is a dibasic acid, forming two classes of salts, viz., acid and normal sulphites.

Tests.—(1.) Its brimstone odor.

(2.) *Starch and iodic acid.* The SO_2 reduces the iodic acid, the free iodine turning the starch blue.

Uses.—In *the arts* it is employed as a bleaching agent for straw, wool and hair, nuts, etc., and also as an '*antichlor*' to get rid of the excess of chlorine in goods bleached by that gas ($SO_2+2H_2O+Cl_2=H_2SO_4+2HCl$). It is also used as an antiseptic, to prevent fermentation, for 'curing' vegetable and fruit extracts, and as a meat preservative. Thus beer and wine casks are first sulphured. Its chief use is in the oil of vitriol manufacture. It is largely employed as a disinfectant.

Sulphuric Anhydride, SO_3 (**S**O_3).

Molecular weight, 80. *Molecular volume*, ▭. *Specific gravity*, 1·95. *Melts at* 65° F. (18·3° C.). *Boils at* 95° F. (35° C.).

Synonyms.—*Sulphur trioxide; Sulphuric oxide; Anhydrous sulphuric acid.*

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Preparation.—(1.) By passing sulphurous anhydride and oxygen either over heated platinized asbestos ($SO_2+O=SO_3$) or through a tube heated to redness, containing oxide of copper and sesquioxide of chromium. (Wöhler.)

(2.) By heating a mixture of sulphuric acid and phosphoric anhydride.

$$H_2SO_4 + P_2O_5 = SO_3 + 2PHO_3.$$

Sulphuric acid + Phosphoric anhydride = Sulphuric anhydride + Metaphosphoric acid.

$$[\mathbf{S}O_2Ho_2 + \mathbf{P}_2O_5 = \mathbf{S}O_3 + 2\mathbf{P}O_2Ho].$$

(3.) By distilling Nordhausen sulphuric acid into an ice-cold receiver (H_2SO_4, $SO_3=H_2SO_4+SO_3$).

(4.) By the action of heat on anhydrous sodic bisulphate (disodic disulphate.)

$$Na_2O,2SO_3 = Na_2SO_4 + SO_3.$$

Sodic bisulphate. = Sodic sulphate + Sulphuric anhydride.

$$\left[\begin{matrix}\mathbf{S}O_2Nao\\ O\\ \mathbf{S}O_2Nao\end{matrix}\right. = \mathbf{S}O_2Nao_2 + \mathbf{S}O_3\Big].$$

Properties.—(*a.*) *Sensible and Physical.* A white, odorless, asbestos-like body, capable of being moulded with the fingers. It has a specific gravity of 1·95. It melts at 65° F. (18·3° C.), and boils at 95° F. (35° C.). It liquefies by exposure to air, and is decomposed by heat into oxygen and sulphurous anhydride.

(*β.*) *Chemical.* It is not acid to dry litmus. It does not burn the dry skin. It dissolves sulphur, forming with it definite compounds. It has a great affinity for moisture, fuming in the air, and hissing when dropped into water, instantly forming sulphuric acid, which cannot, after combination, be separated into water and the anhydride. With ammonia gas it forms ammonic sulphamate.

SULPHURIC ACID, H_2SO_4 ($\mathbf{S}O_2HO_2$.)

Molecular weight, 98. *Molecular volume,* .

Synonyms.—*Vitriolic acid; Oil of Vitriol; Oil of Sulphur; Vitriol; Spirit, or Essence of Vitriol; Dihydric Sulphate; Protohydrate of Sulphuric acid.*

History.—Probably known to Geber in the 8th century. It is mentioned by Basil Valentine (15th century), and was fully and accurately described by Dornœus in 1570.

Natural History.—(*a.*) In the *mineral* kingdom it is found in a free state in the "vinegar springs" of volcanic districts, and largely in combination with lime, etc. (*β.*) In the *vegetable* kingdom it is found combined with alkalies in the juices of plants; and (*γ.*) in the *animal* kingdom it is found to a small extent free, as in the salivary secretions of certain animals (Dolium Galea, 2·7 per cent.), and to a large extent in combination.

Preparation.—(1.) Either by the oxidation of sulphur by boiling

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it in aqua regia, or by its exposure to air in the presence of water ($S_2+3O_2+2H_2O=2H_2SO_4$), or by the oxidation of sulphurous acid, either by exposure to air or oxygen ($H_2SO_3+O=H_2SO_4$).

2. By the action of water on sulphuric anhydride ($SO_3+H_2O=H_2SO_4$).

3. By distilling dry ferrous sulphate (green vitriol), prepared by the oxidation of iron pyrites. This is the old plan still adopted at Nordhausen in Saxony. (Basil Valentine.) The acid produced by this process has the formula H_2SO_4,SO_3. Colcothar (Fe_2O_3) is left in the retort after the distillation is complete.

4. By passing *sulphurous anhydride* (SO_2), vapors of *nitric acid* (HNO_3), *steam* (H_2O), and *air* into a leaden chamber, so arranged as to ensure their perfect admixture. A shallow layer of water covers the bottom of the chamber. (Roebuck, 1720.)

(α.) The *sulphurous anhydride* is generated by burning *crude sulphur* or *pyrites* (which contains 30 to 35 per cent. of sulphur), or the *spent oxide of gas works* (which often contains 40 to 60 per cent. of sulphur).

(β.) The *nitric acid* is generated by the action of sulphuric acid on sodic nitrate.

(γ.) The *steam* is derived from a special water boiler.

(δ.) The *air* is provided in due quantity by maintaining a constant current through the leaden chamber.

Roughly the changes that occur may be stated as follows:—The nitric acid oxidizes the sulphurous anhydride, thereby converting it into sulphuric acid. The nitric acid (HNO_3) becomes, by constantly parting with its oxygen, nitric oxide (N_2O_2). This nitric oxide immediately takes oxygen from the air, and becomes nitric peroxide (N_2O_4), which is again capable of converting fresh sulphurous anhydride into sulphuric acid. Thus theoretically a small quantity of nitric acid vapor in the presence of air, will convert an indefinite quantity of sulphurous anhydride into sulphuric acid, the N_2O_2 merely acting as the carrier of oxygen to the SO_2.

The following are the more accurate details of the reaction:—

(α.) The sulphurous acid is first oxidized by the nitric acid, nitric peroxide being set free.

$$SO_2+2HNO_3=H_2SO_4+N_2O_4.$$

(β.) In the presence of steam the N_2O_4 becomes nitric acid (HNO_3), and nitric oxide (N_2O_2).

$$3N_2O_4+2H_2O=4HNO_3+N_2O_2.$$

(γ.) The HNO_3 thus formed, instantly oxidizes more sulphurous anhydride, and the N_2O_2 takes oxygen from the air, becoming N_2O_3 and N_2O_4, which also oxidizes the SO_2, N_2O_2 being again formed.

$$N_2O_3+SO_2+H_2O=H_2SO_4+N_2O_2.$$

This N_2O_2 again becomes N_2O_3, and N_2O_4 and so on.

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If *little or no steam be present* in the chamber, a white flaky crystalline body ($N_2O_3,2SO_3$?) is formed, produced by the direct combination of nitrous anhydride or nitric peroxide, with oxygen and sulphurous anhydride. When this falls into the water at the bottom of the chamber, it is decomposed, sulphuric acid being produced, and nitric oxide set free. This latter coming into contact with the air, immediately becomes N_2O_4, and again forms fresh flakes of this white crystalline body by combining with sulphurous anhydride. But when *steam is present*, this white body is not formed, but the sulphuric acid is at once produced, and falls as a fine spray into the water.

Properly, nothing should escape from the leaden chamber, except atmospheric nitrogen. Such theoretical accuracy is not, however, of practical attainment. To guard against loss and nuisance, the outlet of the leaden chamber is usually provided with two coke scrubbers. The first of these is kept moist with sulphuric acid to retain the nitric oxide, whereby what is called nitrous sulphuric acid is formed, and from which by heat the nitrous fumes are driven back again into the leaden chamber. In the second scrubber the coke is moistened with water, the liquor from which is allowed to flow on to the floor of the leaden chamber.

When the acid in the chamber has a gravity of from 1·45 to 1·6 it is drawn off, inasmuch as if it were allowed to become of greater concentration it would dissolve nitric oxide. This forms *chamber acid*, and is used in the salt cake manufacture. The chamber acid is concentrated first of all by evaporation in leaden pans until it has a gravity of 1·72, beyond which the acid would seriously affect the lead. This forms *the brown acid* of commerce, and is used in the manufacture of superphosphate, and for other rough purposes. It is afterwards distilled in glass or platinum vessels (the weak distillate being used for the leaden chamber) until the acid in the retort has a gravity of 1·842. This forms the English oil of vitriol, or O.V.

Varieties.—The anhydride forms four definite compounds with water.

(1.) *Nordhausen sulphuric acid*, or *fuming oil of vitriol* (H_2SO_4,SO_3). This is prepared by the distillation of green vitriol. Specific gravity, 1·9. It is used for dissolving indigo.

(2.) *Oil of vitriol*, or *true sulphuric acid* (H_2SO_4). This cannot be prepared by merely boiling down a weak acid, the acid thus obtained always having the composition $H_2SO_4,\frac{1}{12}H_2O$, or $12SO_3,13H_2O$. By exposing this strong acid, however, to a freezing mixture, the acid of the formula H_2SO_4 crystallizes out. These crystals melt at 51° F. (10·5° C.), and boil at 640° F. (470° C.), when the liquid gives off sulphuric anhydride, the resulting acid solution having the formula $12SO_3,13H_2O$.

(3.) *Glacial sulphuric acid* (H_2SO_4,H_2O). This is prepared by cooling an acid of specific gravity 1·78 to 47° F. (8·3° C.), when rhombic crystals

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of H_2SO_4,H_2O separate. It boils at 400° F. (205° C.), giving off a weaker acid.

(4.) *Graham's acid* ($H_2SO_4,2H_2O$).—This is prepared by evaporating a dilute acid 'in vacuo' at 212° F. (100° C.), until it ceases to lose weight. Specific gravity, 1·62. It boils at 379° F. (193° C.).

These facts are tabulated by Miller as follows:—

	Formula.	Fusing point.		Boiling point.		Specific Gravity.
		°C.	°F.	°C.	°F.	
Sulphuric anhydride	SO_3	18·3	65	35	95	1·95
Nordhausen sulphuric acid ..	H_2SO_4,SO_3	35·0	95	52·2	126	1·9
True sulphuric acid, Oil of vitriol	H_2SO_4	10·5	51	338	640	1·848
Glacial acid	H_2SO_4,H_2O	8·3	47	205	400	1·780
Graham's acid	$H_2SO_4,2H_2O$			193	379	1·620

Impurities, and Tests for the Impurities of Sulphuric Acid.

(1.) *Compounds of Oxygen and Nitrogen* (derived from the nitric acid used in the manufacture).

Tests. — (α.) Turns ferrous sulphate an olive green color. (β.) Bleaches dilute indigo.

(2.) *Sulphurous Acid* (derived from the unoxydised SO_2 in the chamber).

Test.—Sulphuretted hydrogen is set free when zinc is added to the acid.

(3.) *Arsenic* (derived from the pyrites).

Test.—(α.) Marsh's test. (β.) Neutralise the acid with potassic carbonate, acidulate with hydrochloric acid, and pass sulphuretted hydrogen through the solution, when the arsenic will be precipitated as a yellow sulphide (orpiment).

(4.) *Lead* (derived from the leaden chamber).

Test.—Mix the acid with about 10 times its bulk of water, when the lead sulphate, which is insoluble in a weak acid, will be precipitated. Boil the precipitate in a solution of sodic carbonate; filter; test one-half of the filtrate with potassic iodide, and the other half with sulphuretted hydrogen.

(5.) *Saline Impurities* (derived either from the nitre, or else purposely added to increase the gravity of the acid).

Test.—Evaporate to dryness for residue.

(6.) *Carbonaceous Matter* (derived from the accidental admixture of the acid with organic matter).

Test.—The color of the acid.

Purification of Sulphuric Acid.

Dilute 1 part of the acid with 5 parts of water. Pass sulphuretted hydrogen through the mixture for 5 or 6 hours. Allow the solid

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impurities to subside, and syphon off the clear liquor. Mix this with a teaspoonful of common salt, and distil, rejecting the first portion that passes over.

Properties.—(α.) *Sensible.*—An oily liquid, without color or smell when pure, but ordinarily more or less colored, from the presence of organic matter. It is an intensely corrosive poison. The Nordhausen acid differs from the other acids by fuming in the air, owing to the separation of a minute trace of sulphuric anhydride.

(β.) *Physical.*—The Nordhausen acid has a gravity of 1·9. Different acids have different gravities, depending on their respective strengths. (*See* Table II. in Appendix.)

Action of Heat.—The *boiling point* of the acids vary. *Nordhausen acid* boils at 126° F. (52·2° C.); *English acid*, at 640° F. (338° C.); the *brown acid*, at 435° F. (224° C.); and *chamber acid*, at 348° F. (175·5° C.). All the acids may be frozen by a cold somewhere about —29° F. (—34° C.), but they require a temperature considerably above this for their re-liquefaction.

The acid does not volatilise at the ordinary temperature of the air. Hence, when a dilute acid is dropped on cloth, it becomes concentrated owing to the gradual evaporation of the water. By warming the cloth before the fire the acid on the fabric may be rendered so concentrated that it chars the cloth.

When the vapour of sulphuric acid is heated it is dissociated, that is, partially decomposed, into SO_3 and H_2O.

The specific gravity of the vapor just above the boiling point of the acid is 2·15, which would represent 2 volumes of H_2O and 2 volumes of SO_3 condensed into 3 volumes; but when the heat is increased to 878° F. (470° C.), these 3 volumes are found to occupy 4 volumes, the vapor, at this higher temperature, having a gravity of 1·692.

When the acid is dropped upon, or the vapor is passed over red-hot platinum, steam, sulphurous anhydride and oxygen are formed. By the action of water the steam and sulphurous acid may be absorbed, and the oxygen obtained in a pure state. (*See* page 57.)

(γ.) *Chemical.*—Sulphuric acid is very acid to litmus. The strong acid when cold, acts feebly on the metals, but when boiled in contact with them (excepting in the case of gold, platinum, iridium and rhodium) it undergoes decomposition, sulphurous anhydride being evolved, and a sulphate of the metal formed ($M'' + 2H_2SO_4 = M''SO_4 + SO_2 + 2H_2O$). When a weak acid is poured on the more oxidizable metals (such as zinc, iron, etc.) hydrogen is evolved, and a sulphate of the metal formed ($Zn + H_2SO_4 = H_2 + ZnSO_4$).

Sulphuric acid evolves oxygen when added to metallic peroxides, but with all oxides it forms sulphates. The concentrated acid is also decomposed when boiled with charcoal or sulphur, sulphurous anhydride being set free.

Its affinity for water is very great. It was found (April, 1870)

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that 100 grains of acid (Sp. Gr. 1·842) freely exposed to the air in a basin, absorbed 120 grains of water in four days, its bulk being thereby increased threefold, and its density lowered to 1·340. The absorption of water, however, by larger quantities is not in like proportion:—1,000 grains of the same acid freely exposed to the air in a similar manner, only absorbed 232 grains of water in 24 hours, 430 grains in 48 hours, 580 grains in 72 hours, 690 grains in 96 hours, and 770 grains in 120 hours. The acid finally had a specific gravity of 1·310, which is the point of dilution at which both weak and strong solutions of the acid arrive when exposed to the air. Moreover, the charring of organic bodies, such as sugar, produced by the action of the acid, is due to this affinity for water.

A great rise of temperature, and consequent condensation, occurs when sulphuric acid is mixed with water. The heat produced is a little greater when the water is poured into the acid than when the acid is poured into the water.

Table showing the Heat and Condensation resulting from various Mixtures of Sulphuric Acid and Water. Temperature of Day, 22·22° C. (72° F.).

Sp. Gr. of the Acid used.	Weight of Acid used, in Grains	Bulk of Acid used.	Weight of Water used, in Grains.	Bulk of Water used.	Temperature produced.		Bulk of Resulting Fluid when cold.	Sp. Gr. of Resulting Fluid.
					°F.	°C.		
1·840	3000	℥ iij & ʒ vj	1000	℥ ij & ʒ ij	266	130·00	℥ v	1·616
1·840	2000	℥ iiss	do.	do.	252	122·20	℥ iv	1·548
1·840	1000	℥ j & ʒ ij	do.	do.	210	98·88	℥ iij	1·390
1·840	500	ʒ v	do.	do.	198	92·22	℥ ij & ʒ ivss	1·245
1·840	250	ʒ iiss	do.	do.	130	54·44	℥ ij & ʒ iij	1·136
1·616	1616	℥ ij & ʒ ij	do.	do.	119	48·33	do.	1·282
1·548	1548	do.	do.	do.	108	42·22	do.	1·246
1·390	1390	do.	do.	do.	95	35·00	do.	1·170
1·245	1245	do.	do.	do.	81	27·22	do.	1·074
1·138	1138	do.	do.	do.	78	25·55	do.	1·055

This table explains the use of the acid in the laboratory as a dessicating and dehydrating reagent.

Certain *organic bodies*, such as starch and cellulose, are carbonized by the strong acid, whilst dilute acids convert them into grape sugar. The acid coagulates albumen, forming with it, as with other organic bodies, definite chemical compounds which are insoluble.

Sulphuric acid is a powerful dibasic acid, and displaces other acids, such as nitric, hydrochloric acids, etc., from their compounds. It forms two classes of sulphates, viz., an acid sulphate, where one hydrogen only is replaced by a metal ($M'HSO_4$), and a normal sulphate, where both hydrogens are replaced by a metal or metals ($M'SO_4$ or $M''SO_4$.)

Tests.—(1.) *Taste.* The solution is perceptibly sour when it contains 1-1000th part of anhydrous acid.

(2.) *Action on Litmus.* The reddening of blue litmus is distinct when 1 part of anhydrous acid is diluted with 6,000 of water.

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(3.) *Calcic Chloride* gives a copious white precipitate, insoluble in dilute nitric and hydrochloric acids. A turbidity is distinctly apparent when the solution contains only 0·014 per cent. of acid.

(4.) *Plumbic Acetate* gives a white precipitate, insoluble in dilute acids.

(5.) *Baric Chloride* (or baric nitrate) gives a white precipitate, insoluble in free acids and in caustic alkalies. The turbidity is apparent with a solution consisting of 1 part of acid in 62,500 of water.

The baryta salt must never be added to a *neutral* or to an *alkaline* solution, otherwise carbonic, phosphoric, oxalic acids, etc., may be precipitated, all of which are, however, soluble in nitric or hydrochloric acid. To prove that the precipitate is a baric sulphate, it must be collected and dried, and mixed with about four times its bulk of powdered wood charcoal. This mixture is then to be heated to redness for some time in a platinum crucible. By this means $BaSO_4$ will be reduced to BaS. Add to the cold residue a few drops of dilute hydrochloric acid, and apply heat, when sulphuretted hydrogen will be generated, which may be known by its blackening moistened lead paper.

(6.) *Nitrate of Strontia* gives a white precipitate, partially soluble in water and in dilute acids.

(7.) If sulphuric acid be gently heated in a test tube with some pieces of wood, copper, or mercury, etc., sulphurous anhydride is evolved, and may be known by its imparting a blue tint to a piece of starch paper moistened with iodic acid.

(8.) A trace of *veratria* added to a drop of *concentrated* acid, produces first a yellow and afterwards a crimson-red solution.

(9.) Paper is carbonized by the *strong* acid. If the acid be dilute, wet a piece of white paper at one spot and heat before a fire. As soon as the acid becomes sufficiently concentrated by evaporation, the paper will turn black.

Uses.—*In the arts and manufactures* numberless. *In medicine* the following preparations are officinal:—*Acidum Sulphuricum*, B.P., Sp. Gr., 1·84=96·8 per cent. of H_2SO_4; *Acidum Sulphuricum dilutum*, B.P., Sp. Gr., 1·394=13·64 per cent. of H_2SO_4; *Acidum Sulphuricum Aromaticum*, B.P., of similar strength to the dilute acid, but containing ginger and cinnamon.

Hyposulphurous Acid, $H_2SO_2(SHO_2)$.

Synonym.—*Hydrosulphurous Acid.*

[NOTE.—H_2SO_2 is the true hyposulphurous acid; $H_2S_2O_3$, which is ordinarily called hyposulphurous acid, is really thiosulphuric or sulpho-sulphuric acid.

History.—Discovered by Schützenberger.

Preparation. (1.) By dissolving zinc in sulphurous acid. (Note:—No hydrogen is evolved during the reaction).

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H_2SO_3	+	Zn	=	H_2SO_2	+	ZnO.
Sulphurous acid	+	Zinc	=	Hyposulphurous acid	+	Zincic oxide.
[$\mathbf{S}OHo_2$	+	Zn	=	$\mathbf{S}Ho_2$	+	ZnO].

(2.) By decomposing sodic hyposulphite ($NaHSO_2$) with oxalic acid.

Properties.—The yellow solution of the acid thus formed bleaches powerfully, its bleaching action depending on its reducing power. It throws down mercury and silver from their solutions. It rapidly decomposes by absorbing oxygen.

Thiosulphuric Acid, $H_2S_2O_3$($\mathbf{S}S''OHo_2$?).

Synonyms.—*Hyposulphurous acid*: *Sulpho-sulphuric acid*; *Dithionous acid.*

The free acid has never been obtained. The salts are prepared either (1) by boiling sulphur with a solution of a sulphite ($Na_2SO_3+S=Na_2S_2O_3$); or (2) by boiling sulphur with an alkaline hydrate ($3CaO,H_2O+12S=CaS_2O_3+2CaS_5+3H_2O$). A further quantity of CaS_2O_3 is formed from the CaS_5 in the latter reaction, by exposing the solution to the air ($CaS_5+3O=CaS_2O_3+S_3$).

Calcic Thiosulphate ($CaS_2O_3,6H_2O$) is found in large quantities in the refuse lime of gas works, and also in the refuse from the ball soda of the alkali works.

The Sodic Thiosulphate or **Hyposulphite**, as it is called, is largely used by the dyer as an antichlor, as well as in photography and metallurgy, on account of its power of dissolving the insoluble argentic haloid salts, by forming with them double soluble salts. It is prepared either (1) by treating a solution of sodic sulphide with sulphurous acid; or (2) by digesting together sulphur and sodic sulphite, or (3) by exposing the calcic sulphide (tank waste or soda waste) of the gas or alkali works to the air, whereby a calcic hyposulphite is formed by oxidation, from which 'hyposulphite of soda' may be prepared by the action of sodic carbonate. The thiosulphates will not yield the free acid by the action of a stronger acid, on account of the ease with which they are decomposed into sulphur and sulphurous acid ($H_2S_2O_3=S+H_2SO_3$).

To distinguish thiosulphuric from sulphurous acid note that—

(1.) On adding an acid to a thiosulphate, sulphur is precipitated, and sulphurous anhydride is evolved.

(2.) Thiosulphuric acid dissolves argentic chloride, forming argentic sodic thiosulphite ($NaAgS_2O_3$).

(3.) A salt of ruthenium, rendered alkaline with ammonia, turns thiosulphuric acid a deep red color.

The sodic hyposulphite, when heated, first loses water, and is then decomposed ($4Na_2S_2O_3=3Na_2SO_4+Na_2S_5$).

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Dithionic Acid, $H_2S_2O_6$=162. ($'S^{V}_{2}O_4Ho_2$).

Synonyms.—*Hyposulphuric acid.*

Preparation. (α.) *A manganous dithionate* (MnS_2O_6) is first prepared by passing SO_2 through cold water containing manganic peroxide in suspension ($MnO_2+2SO_2=MnS_2O_6$).

(β.) *A baric dithionate* (BaS_2O_6) is then prepared by acting on the manganous dithionate with baric sulphide ($MnS_2O_6+BaS=MnS+BaS_2O_6$).

(γ.) *Dithionic acid* is now liberated by the action of sulphuric acid (in equivalent proportion) on the baric dithionate ($BaS_2O_6+H_2SO_4=BaSO_4+H_2S_2O_6$).

Properties.—The acid, when fully concentrated by evaporation 'in vacuo,' has a specific gravity of 1·347, and forms a colorless acid liquid without odor. If the concentration be attempted beyond this point, or if heat be applied to the acid solution, it breaks up into sulphuric acid and sulphurous anhydride ($H_2S_2O_6=H_2SO_4+SO_2$). When exposed to the air, dithionic acid rapidly forms sulphuric acid.

All the dithionates (hyposulphates) are soluble in water, and are decomposed by heat in the presence of hydrochloric acid, sulphurous anhydride being evolved *without the deposition of any free sulphur.* This distinguishes them from other sulphur compounds.

Trithionic Acid ($H_2S_3O_6$=194).

Synonyms.—*Dihydric trithionate; Sulphodithionic acid; Sulphuretted hyposulphuric acid.*

History.—Discovered by Langlois.

Preparation of the free acid. (α.) A potassic trithionate ($K_2S_3O_6$) is first prepared by digesting acid potassic sulphite ($KHSO_3$) with powdered sulphur. Thus—

$$12KHSO_3 + S_2 = 4K_2S_3O_6 + 2K_2SO_3 + 6H_2O.$$

Hydric potassic sulphite + Sulphur = Potassic trithionate + Potassic sulphite + Water.

$$[12\mathbf{S}OHoKo + S_2 = 4\left\{\begin{matrix}\mathbf{S}O_2Ko\\ S\\ \mathbf{S}O_2Ko\end{matrix}\right. + 2\mathbf{S}OKo_2 + 6\mathbf{O}H_2.$$

(β.) On dissolving the crystals of potassic trithionate ($K_2S_3O_6$) in water and adding perchloric or hydrofluosilicic acid, the potash is precipitated, and a solution of the acid obtained.

Properties.—The acid crystallizes in four-sided prisms. It rapidly decomposes into sulphurous anhydride, sulphurous acid, and free sulphur ($4H_2S_3O_6=6SO_2+4H_2SO_3+S_2$).

The *trithionates* are soluble unstable salts, and are easily decomposed by heat into sulphates, sulphurous anhydride being evolved with the deposition of free sulphur. They give with mercurous nitrate a *black* precipitate, with mercuric nitrate a *white* precipitate, and with argentic nitrate a *yellow* precipitate, which in time becomes black.

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Tetrathionic Acid ($H_2S_4O_6 = 226$).

Synonyms.—*Dihydric Tetrathionate; Disulpho-dithionic acid; Bisulphuretted hyposulphuric acid.*

History.—Discovered by Fordos and Gélis.

Preparation of the free acid. (α.) Baric tetrathionate is formed by adding iodine to baric hyposulphite (thiosulphate) ($2BaS_2O_3 + I_2 = BaI_2 + BaS_4O_6$).

(β.) *Tetrathionic acid* is now set free by decomposing baric tetrathionate with its exact equivalent of sulphuric acid.

Properties.—The acid is very unstable. When heated, a solution of sulphuric acid is formed, sulphurous anhydride is evolved, and free sulphur is deposited ($H_2S_4O_6 = H_2SO_4 + SO_2 + S_2$). The potassic salt may be recognised by the separation of sulphur when heated with potassic sulphide ($2K_2S_4O_6 + 2K_2S = 4K_2S_2O_3 + S_2$).

Pentathionic Acid ($H_2S_5O_6$=258).

Synonyms.—*Trisulphodithionic acid; Trisulphuretted hyposulphuric acid.*

History.—Discovered by Wackenroder.

Preparation.—By passing sulphuretted hydrogen through a solution of sulphurous acid ($10SO_2+10H_2S=2H_2S_5O_6+5S_2+8H_2O$).

The clear solution is to be concentrated *in vacuo* over oil of vitriol.

Properties.—The solution thus obtained has a specific gravity of 1·6, and is acid, bitter and tolerably permanent. Concentrated beyond this gravity it rapidly decomposes. By heat it is resolved into sulphuric acid, sulphuretted hydrogen, sulphurous anhydride, and free sulphur ($2H_2S_5O_6=H_2SO_4+H_2S+4SO_2+2S_2$).

The polythionic acids, as an aid to memory, are represented by Bloxam as derived from oil of vitriol by successive additions of sulphurous anhydride and sulphur: thus

Oil of vitriol	H_2SO_4	$=H_2SO_4$
Thiosulphuric acid	$H_2SO_4+SO_2$	$=H_2S_2O_6$
Trithionic ,,	$H_2SO_4+SO_2+S$	$=H_2S_3O_6$
Tetrathionic ,,	$H_2SO_4+SO_2+S_2$	$=H_2S_4O_6$
Pentathionic ,,	$H_2SO_4+SO_2+S_3$	$=H_2S_5O_6$.

Note the following reactions:

The *sulphates* with concentrated sulphuric acid (hot or cold) emit no odor.

The *sulphites* with dilute sulphuric acid (cold) emit an odor of SO_2.

The *hyposulphates* (dithionates) with dilute sulphuric acid (cold) emit no odor, but when heated emit the odor of SO_2.

The *thiosulphates* (hyposulphites) with dilute sulphuric acid (cold) emit an odor of SO_2, with the deposition of free sulphur.

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COMPOUNDS OF SULPHUR AND THE HALOIDS.

Compounds of Sulphur and Chlorine.

1. Sulphur chloride ... ... S_2Cl_2
2. Sulphur dichloride ... ... SCl_2
3. Sulphur tetrachloride ... ... SCl_4 ?

Sulphur Chloride (S_2Cl_2 or $\left\{\begin{matrix}SCl.\\SCl.\end{matrix}\right)$

Molecular weight, 135. *Molecular volume*, □□. *Specific gravity*, 1·68; *of vapor*, 4·7.

Preparation.—By passing chlorine into melted sulphur and collecting the product in a dry cold receiver.

Properties.—A yellow volatile liquid (Sp. Gr. 1·68), fuming in the air, and emitting a pungent odor. The specific gravity of the vapor is 4·7. It is decomposed by water into sulphurous, hydrochloric, and thiosulphuric acids, and free sulphur (electro-positive). It dissolves sulphur freely; hence its use in the manufacture of vulcanised rubber. It acts powerfully on mercury.

Sulphur Dichloride (SCl_2=103).

Preparation.—By saturating the sulphur chloride with chlorine.

Properties.—A deep red liquid. It is decomposed by heat and by the sun's rays ($2SCl_2=S_2Cl_2+Cl_2$).

Sulphur Tetrachloride, SCl_4 (?)

This compound is not known in a free state, and there is some doubt even as to its existence in combination.

COMPOUNDS OF SULPHUR WITH BROMINE AND IODINE.

Compounds of *sulphur* with *bromine and iodine* similar to the chlorine compounds are believed to exist. A **Sulphur Diiodide** (SI_2), a body produced by direct combination, and a **Sulphur Subiodide** (S_2I_2) are the compounds best known.

COMPOUNDS OF SULPHUR, OXYGEN AND THE HALOIDS.

Thionyl Chloride ($SOCl_2$) is an analogous compound to sulphurous acid, two of hydroxyl being displaced by two of chlorine ($SOHo_2$—$SOCl_2$).

Preparation.—By acting on phosphoric chloride with sulphurous anhydride. (Schiff.)

Properties.—A colorless, pungent liquid of great refractive power; specific gravity, 1·675; boils at 172·4° F. (78° C.). It is decomposed by water into sulphurous anhydride and hydrochloric acid. It forms *thionamide* with ammonia.

Sulphuryl Dichloride (SO_2Cl_2). **Preparation.**—By exposing a mixture of sulphurous anhydride and chlorine to sunlight.

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Properties.—A colorless liquid, specific gravity, 1·66; decomposed by water into sulphuric and hydrochloric acids.

Sulphuryl Dibromide (SO_2Br_2), a white, crystalline body, *Chlorosulphuric oxide* ($S_2O_5Cl_2$), a colorless oily liquid, and *Sulphuryl hydroxyl chloride* (SO_3HCl) have also been described.

COMPOUNDS OF SULPHUR AND PHOSPHORUS.

Phosphorus protosulphide	... P_2S.
Phosphorus sesquisulphide	... P_2S_3.
Phosphorus pentasulphide	... P_2S_5.

Phosphorus Protosulphide (P_2S) is a yellow, oily liquid, and is not decomposed by water.

Phosphorus Sesquisulphide (P_2S_3) is prepared by the action of sulphuretted hydrogen on phosphorous chloride ($2PCl_3 + 3H_2S = P_2S_3 + 6HCl$). It is a yellow crystalline solid, easily decomposed by water.

Phosphorus Pentasulphide (P_2S_5) is a body easily decomposed by water.

Other compounds, as P_4S, P_4S_3, P_2S_{12}, have also been described.

SELENIUM (Se_2).

Atomic weight, 79·5. *Molecular weight*, 159. *Molecular volume*, □. *Relative weight*, 79·5. *Specific gravity of solid*, 4·788; *of vapor*, 5·68; *Atomicity*; *Hexad* ($\mathbf{Se}^{vi}O_2HO_2$); *Tetrad* ($\mathbf{Se}Cl_4$); *Dyad* ($\mathbf{Se}H_2$).

History.—Discovered by Berzelius (1817) in the refuse of a sulphuric acid factory.

Natural History.—It is found native, but occurs chiefly in combination, as a selenide of copper, iron, silver, etc. It also occurs as an impurity in native sulphur (seleniferous sulphur).

Preparation.—By the action of a mixture of nitric and sulphuric acids on the seleniferous deposits of vitriol works, a solution containing selenious and selenic acids is formed. The selenic acid present in the solution is now to be reduced to selenious acid by the action of hydrochloric acid ($H_2SeO_4 + 2HCl = H_2SeO_3 + H_2O + Cl_2$). From this solution of selenious acid, the selenium may be precipitated by a current of sulphurous anhydride ($2H_2SeO_3 + 2H_2O + 4SO_2 = 4H_2SO_4 + Se_2$).

Varieties.—Like sulphur, selenium is found in various allotropic forms.

(a.) The *amorphous form*, prepared as described above, consists of red flakes, which are ductile when melted. It has no taste or smell, and is a bad conductor of heat and electricity.

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(β.) A *black vitreous form*, prepared by first heating the preceding amorphous variety to 212° F. (100° C.), and then rapidly cooling. It has a specific gravity of 4·3. It is insoluble in carbonic disulphide.

(γ.) A *crystalline form*, prepared by heating the vitreous form to 204·8° F. (96° C.) It has a specific gravity of 4·8. Its color is bluish grey (σελήνη, the moon).

Properties.—(α.) *Physical.* The color of selenium is either red, black, or bluish grey, according to the variety. Solid selenium has neither taste nor smell, but the vapor has the odor of putrid horseradish. It conducts heat and electricity badly, but its electric conductivity is greatly increased by exposure to direct sunlight. It is insoluble in water. It fuses readily, and boils below a red heat, giving off a yellow vapor, which, like that of sulphur, expands anomalously (*see* page 145).

(β.) *Chemical.* Selenium vapor burns with a blue flame, forming SeO_2. By boiling with nitric acid, selenious acid is formed. Selenium is soluble in sulphuric acid, forming a green solution, from which the selenium may be thrown down by the addition of water.

COMPOUNDS OF SELENIUM AND OXYGEN, ETC.

Selenious anhydride	...	SeO_2.
Selenious acid	...	H_2SeO_3, or $SeOHo_2$.
Selenic acid	...	H_2SeO_4, or SeO_2Ho_2.

Selenious Anhydride (SeO_2).

Preparation.—By burning selenium in oxygen, or by boiling it with nitric acid.

Properties.—A white, deliquescent, crystalline substance, soluble in water, forming selenious acid (H_2SeO_3, or $SeOHo_2$). This acid may also be obtained as a white solid. On adding iron, zinc, sulphurous acid, or sulphuretted hydrogen to a solution of selenious acid, selenium will be precipitated.

Selenic Acid (H_2SeO_4, or SeO_2Ho_2.)

This acid is not known as an anhydride.

Preparation.—(1.) (α.) A *potassic seleniate* is first formed by fusing together nitre and selenium ($4KNO_3 + Se_2 = 2K_2SeO_4 + 2N_2O_2$). (β.) A *plumbic seleniate* is then prepared by the action of plumbic nitrate on a solution of potassic seleniate. (γ.) On treating plumbic seleniate with sulphuretted hydrogen, an insoluble plumbic sulphide and a solution of selenic acid are formed.

(2.) By the action of chlorine or manganic peroxide on selenious acid.

Properties.—A colorless, syrupy, hygroscopic liquid, evolving considerable heat when mixed with water. It may be concentrated until it has a specific gravity of 2·6. At a temperature of 554° F. (290° C.) it is decomposed into selenious acid, water, and oxygen.

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It has no action on platinum, but it oxidizes the metals generally, and even dissolves gold. When heated with hydrochloric acid it is decomposed ($H_2SeO_4+2HCl=H_2SeO_3+H_2O+Cl_2$).

Compounds of Selenium and Chlorine.

Selenium forms two chlorides, viz., a *monochloride* (Se_2Cl_2), a yellow liquid formed by the direct union of selenium and chlorine, and a *tetrachloride* ($SeCl_4$), a white crystalline solid, formed by treating Se_2Cl_2 with an excess of chlorine. On its exposure to moisture an *oxychloride* ($SeOCl_2$) is formed.

The combinations of selenium with the other haloid elements are imperfectly understood.

A *carbonic selenide* (CSe_2) and two *sulphides* (SeS_2 and SeS_3) have been described.

TELLURIUM (Te_2).

Atomic weight, 128. *Molecular weight*, 256. *Relative weight*, 128. *Specific gravity of solid*, 6·2; *of vapour* (*at* 2,534°F), 9·0. *Atomicity, hexad* (H_2TeO_4); *tetrad* ($TeCl_4$); *dyad* (TeH_2).

History.—Discovered by Müller (1782). Its elementary nature was determined by Klaproth (1798), and the body named by him Tellurium (*Tellus*).

Natural History.—It is a very rare substance, but is found both in a free state, and also combined with bismuth, lead, silver, etc.

Properties.—(*α.*) *Physical.* A pinkish-white metallic-looking body, crystalline (rhombohedral), and very brittle. It fuses between 800° and 900° F. (426° and 482° C.), and becomes, at a higher temperature, a yellow gas. It conducts heat and electricity badly. It is insoluble in water. When taken internally it imparts a peculiar garlic odor to the breath.

(*β.*) *Chemical.* Tellurium burns, when heated in air, with a blue flame, yielding TeO_2. It does not form, like the metals, a true basic oxide. Its solution in sulphuric acid, which is of a purple-red color, yields a precipitate of tellurium when treated with water.

Compounds of Tellurium and Oxygen, etc.

Tellurous oxide	...	...	TeO_2.
Tellurous acid	...	...	H_2TeO_3, or $\mathbf{Te}OHo_2$.
Telluric oxide	...	...	TeO_3.
Telluric acid	...	...	H_2TeO_4, or $\mathbf{Te}O_2Ho_2$.

Tellurous Oxide (TeO_2.)

This oxide occurs native as tellurite. It is a white, fusible crystalline body. It forms a yellow glass when hot, which becomes white

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on cooling. At a greater heat it sublimes unchanged. It is slightly soluble in water, forming *tellurous acid* (H_2TeO_3, or $TeOHo_2$), which forms two classes of salts, viz.—*neutral* (M_2TeO_3), and *acid* ($M'HTeO_3$), tellurites.

Telluric Oxide (TeO_3).

Telluric oxide is a yellow, solid body, insoluble in water and in acids. It is prepared by the action of heat on *telluric acid* (H_2TeO_4).

Telluric Acid (H_2TeO_4, or TeO_2Ho_2).

Telluric acid is prepared by first forming a potassic tellurate by the fusion of tellurium with nitre. On adding baric chloride to the solution, and decomposing the baric tellurate formed with sulphuric acid, a solution of telluric acid is obtained. The solution, after the baric sulphate has been filtered off, yields crystals having the composition $H_2TeO_4,2H_2O$, from which the two molecules of water may be expelled by heat. It forms salts called tellurates, which are mostly insoluble.

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CHAPTER VIII.

CARBON—BORON—SILICON.

CARBON:—Compounds of Carbon and Oxygen—Compounds of Carbon and the Haloids—Compounds of Carbon with Oxygen and the Haloids—Compounds of Carbon and Sulphur. BORON:—Boracic acid—Compounds of Boron with Nitrogen, the Haloids, and Sulphur. SILICON:—Compounds of Silicon with Oxygen, the Haloids, Nitrogen, and Sulphur.

CARBON (C=12).

Atomic weight, 12. *Atomicity, dyad* (CO); *tetrad* (CO_2—CH_4). *Vapor density, unknown.*

Synonym.—*Charcoal.*

History.—Carbon has been known from very early times. Eresius (300 B.C.) described the method of preparing it from wood, and in Pliny's time it constituted the common fuel. In A.D. 1694 the Florentine academicians burnt the diamond by the sun's rays. In 1775–6 Lavoisier effected its combustion in oxygen, and in 1809 Davy burnt graphite in a similar manner. Thus these bodies respectively, were proved to be pure carbon. Newton, however, had long before this, asserted that the diamond was a combustible body, on account of its high refractive power.

Natural History.—(α.) In the *mineral kingdom* carbon is found in a free state; (1) as the *diamond* in sandstone rocks or mica slate. Its origin is unknown. The ash, consisting of silica and oxide of iron, left after its perfect combustion, is very minute. (2.) As *plumbago*, the ash of which varies from 2 to 5 per cent., and consists of a little quartz mixed with the oxides of iron and manganese. (3.) As *anthracite*, the ash of which varies greatly both in quantity and composition. (4.) Carbon is also found associated (*a*) with *hydrogen* in coal, bitumen, jet, shales, naphtha, and in the paraffines, (*b*) with *oxygen* in *carbonic anhydride*, and (*c.*) with *oxygen and the metals* in the carbonates.

(β.) *In the vegetable kingdom*, carbon forms about 50 per cent. of dry vegetable solids. It is supplied to them by the atmospheric carbonic anhydride which the plant deoxidizes under the influence of solar light. Plants are *deoxidizing* agents, animals are *oxidizing* agents.

(γ.) *In the animal kingdom*, all tissues and products are largely made up of it. Fat contains about 79 per cent.

The chemist roughly proves a body to be of organic origin by the circumstance that it carbonizes when burnt with a limited supply of air.

Varieties.—(1.) *Diamond.*—The diamond crystallizes in cubes or in octahedra with convex faces and rounded edges (lenticular). It

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cannot be produced artificially. Its specific gravity is 3·4. It is usually colorless, but is found at times of a yellow, green, blue, and black tint, the colors being due to mineral matter. It is one of the hardest bodies known (adamant). It has never been melted. It is a non-conductor of electricity, but when heated in the voltaic arc, it swells up and forms a coke-like mass, which conducts electricity freely. Some diamonds are phosphorescent after exposure to intense sunlight. It has a high refracting power: at an angle of 24·15 all light is returned.

It is not affected by the action of nitric acid and potassic chlorate.

A diamond may be known (α) by its *hardness* (scratching hardened steel); (β) by its *gravity*; and (γ) by its *insolubility* in *hydrofluoric acid.*

(2.) *Graphite* ($\gamma\rho\alpha\phi\omega$, I write).—Graphite is found both crystalline (six-sided plates) and in amorphous masses. It has a specific gravity of 2·2. It is greyish-black, with a metallic lustre (*black lead* or *plumbago*). It is unctuous to touch, and, although the minute particles are excessively hard, it nevertheless marks paper when drawn across it. It is a good conductor of electricity.

When plumbago is acted on with a mixture of nitric acid and potassic chlorate it forms '*graphic* or *graphitic acid,* a brown, crystalline body, which swells up when heated, forming '*pyrographitic oxide.*' This latter substance is soluble in nitric acid and potassic chlorate.

(3.) *Amorphous carbon.*—Amorphous carbon has a specific gravity varying from 1·6 to 2·0. Its apparent lightness, such as floating on water, is due to the presence of air in its pores. It is found in various forms, more or less pure, as *e. g.*, (α.) *Coke,* the residue of coal after the gas and volatile matters have been expelled. (β.) *The carbon of gas retorts,* a body resembling graphite in some particulars, but differing in that it does not form "graphic acid" by the action of nitric acid and potassic chlorate. (γ.) *Soot,* the condensed smoke deposited in chimneys. (δ.) *Lampblack,* the unburnt carbon resulting from the combustion of rich hydro-carbons in a limited supply of air. (ϵ.) *Wood charcoal,* the carbon of wood and other vegetable matters. (ζ.) *Animal charcoal* (*ivory black* or *bone black*), the carbon of bone or other animal substances. (η.) *Tinder.*

All these forms, when treated with nitric acid and potassic chlorate, yield brown compounds that are soluble in water.

It has been conjectured, considering the striking differences in the properties of these carbon allotropes, that they consist of dissimilar carbon molecules. The study of their specific heats would suggest that the charcoal molecule consists of two atoms, the graphite of three, and the diamond of four. (Specific heat of *diamond,* ·14687; of *plumbago,* ·2008; of *charcoal,* ·2415.)

Preparation.—(1.) *Diamond.*—The diamond cannot be prepared artificially (Action of phosphorus on chloride of carbon?).

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(2.) *Graphite.*—(α.) By submitting the diamond to an intense heat.

(β.) By dissolving carbon in cast iron. On allowing the mixture to cool slowly, six sided crystalline plates of graphite separate (called "kish").

(γ.) By dissolving away the iron from cast iron, thus leaving the insoluble graphitic carbon.

(δ.) By submitting the various forms of amorphous carbon to the heat of the electric arc.

(3.) *Amorphous carbon.*—(α.) *Coke.* By heating coal in closed iron cylinders, an escape being provided for the gaseous and other volatile matters. The higher the temperature to which the coal is subjected, the more dense the coke. Coke may also be prepared by burning the coal in heaps similar to the preparation of wood-charcoal.

(β.) *Carbon of gas retorts.*—From the decomposition of a portion of the gas or volatile hydro-carbons by the red hot retort, upon which a layer of gas carbon slowly deposits. Its appearance varies according to the temperature at which it is formed.

(γ.) *Soot.*—The condensed smoke of chimneys.

(δ.) *Lampblack.*—By burning certain vegetable matters rich in carbon, such as resin, tar, etc., in a current of air insufficient for complete combustion. The hydrogen being the most combustible portion burns first, and the carbon, for which there is not sufficient air, is collected in chambers covered with coarse cloth.

(ε.) *Wood charcoal.*—(1.) By the distillation of wood in closed retorts. *Acid* fumes are evolved during the process, wood containing little or no nitrogen, charcoal remaining in the retort. (2.) By the slow burning of logs of dry wood arranged in heaps, covered, except round the base of the heap, with turf. In this way, every 100 parts of wood yield about 22 parts of carbon.*

Wood charcoal never consists of pure carbon. The higher the temperature at which the wood is burnt, the smaller the quantity of charcoal formed, but the larger the percentage of carbon that it contains. The "charbon roux" of the French consists of wood imperfectly burnt by the action of superheated steam.

(ζ.) *Animal charcoal.*—By burning bones or other animal matter in closed retorts, when *alkaline* fumes are evolved, from the nitrogen present in the animal matters forming ammonia, animal charcoal remaining in the retort (ivory black).

Properties.—(α.) *Sensible.*—Carbon, in all its forms, is a solid without taste or smell, and, excepting the diamond, of a black color.

* If a piece of wood ($C_6H_{10}O_5$) be burnt in the *open fire*, with free access of air, carbonic acid and water only are produced; but when burnt in a *close vessel*, where the free access of oxygen is prevented, the wood does not truly burn, but simply undergoes destructive distillation; that is, it becomes changed into simpler and more stable products, tar, acetic acid, and wood spirit being amongst the products formed.

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(β.) *Physical.*—The diamond is the hardest substance known, although nearly approached in this respect by crystallized boron. The other varieties of carbon are comparatively soft, although graphite, which may be easily cut with a saw, is said to wear out the instruments rapidly, owing to the extreme hardness of its minute particles.

Carbon is *dimorphous.* It is *cubic* in the diamond, and *six sided* in some varieties of graphite. The other forms of carbon, as well as occasionally graphite, are amorphous. Its specific gravity varies; that of the *diamond* ranges from 3·33 to 3·55; of *graphite,* from 2·0 to 2·35; of *anthracite* and *coke,* from 1·4 to 2, etc.

Action of heat.—Carbon, in all its forms, is believed to be infusible and involatile. It has been noticed, however, that when the carbon points from a large battery are brought into contact in an exhausted receiver, a dark cloud appears, and that a black crystalline body is slowly deposited on the sides of the glass. Further, when pure powdered carbon is exposed to the intense heat of the voltaic arc, it forms a coherent mass as if it had been fused. (Despretz.) The diamond, when heated in the battery, swells up and cakes, although there is no reason to believe that it is capable of vaporisation. Finely-divided carbon conducts heat badly. The diamond is a non-conductor. The other varieties, when "en masse," conduct heat well, the power of conduction increasing with the density.

Carbon, in all its forms, excepting the diamond, is a conductor of electricity. Hence the use of graphite in electrotyping.

Carbon is insoluble in every known liquid.

(γ.) *Chemical.*—Carbon in all its forms is combustible in air and oxygen, yielding as its sole product carbonic anhydride (CO_2). The diamond and graphite are difficult of combustion, but the rest burn easily. In none of its forms is carbon altered by exposure to weather; hence many of its uses.

Action of oxygen.—The action of oxygen on carbon is sometimes, though rarely, manifested at ordinary temperatures. Thus ferric may be changed to ferrous, and mercuric to mercurous salts, by merely shaking up their solutions with powdered charcoal. At high temperatures carbon burns in oxygen, and even in carbonic anhydride, in which latter it appropriates one half of the oxygen ($C+CO_2=2CO$.) Hot charcoal decomposes steam, liberating hydrogen, and setting free, according to the temperature, either carbonic anhydride or carbonic oxide. Its property of combining with oxygen is made use of in extracting the metals from their oxides, carbonic anhydride being set free in the case of oxides easily reduced ($2PbO+C=Pb_2+CO_2$), and carbonic oxide with those difficult of reduction ($ZnO+C=Zn+CO$).

Action of the haloids.—The direct combination of carbon with the haloids cannot be effected, but indirect combination, either by the

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substitution of the haloid elements for hydrogen in, or the addition of the haloid elements to, the hydrocarbons, is of constant occurrence. Thus ethylene (C_2H_4) will combine with bromine to form ethylene dibromide ($C_2H_4Br_2$), which, by successive substitutions of bromine for hydrogen, may ultimately be converted into tetrabromethylene dibromide (C_2Br_6).

Action on nitrogen.—The direct union of carbon with nitrogen cannot be effected; but if nitrogen be passed over a mixture of carbon and potassic carbonate heated to redness, cyanogen (CN) is formed, which unites with the potassium to form potassic cyanide ($K_2CO_3+4C+N_2=2KCN+3CO$.)

Action on sulphur.—Direct union between carbon and sulphur occurs at a high temperature, carbonic disulphide (CS_2) being formed.

Action on hydrogen.—Hydrogen and carbon unite directly at high temperatures, such as the heat of the voltaic arc, forming acetylene (C_2H_2). (Berthollet). During the destructive distillation of organic bodies numerous hydrocarbons are produced (*see* Destructive Distillation).

Action on the metals.—Carbon unites at high temperatures with certain metals, such as iron, manganese, palladium, iridium, etc., forming carbides.

Carbon does not combine with phosphorus.

We may note generally, that carbon exhibits a great indisposition to combine directly with the elements. Hence it is customary to char the ends of stakes, in order to prevent their decay by the action of air and moisture when driven into the ground, and to blacklead metal, so as to prevent its oxidation.

Action of Compounds.—(1.) *Water* has no action on carbon, except at a red heat, when hydrogen, together with carbonic oxide or carbonic anhydride (one or both), are formed ($3H_2O+2C=3H_2+CO+CO_2$).

(2.) *Acids.*—*Sulphuric acid* has no action on carbon, except when heated, when the acid is reduced ($2H_2SO_4+C=CO_2+2SO_2+2H_2O$). *Nitric acid* deflagrates when heated with carbon, the oxides of carbon and the lower oxides of nitrogen being formed. The action of nitric acid and potassic chlorate on the various forms of carbon is as follows:—the diamond is unaffected; graphite is changed into graphic or graphitic acid (graphitic oxide) ($C_{11}H_4O_5$), a yellow silky substance, insoluble in water or in acids, and which, when heated, swells up, and becomes pyrographitic oxide; the amorphous varieties are soluble, forming brown solutions. *Hydrochloric* and *hydrofluoric acids* have no action on carbon; *phosphoric* acid is reduced by it, phosphorus being set free.

(3.) *The fixed alkalies* and the *oxides* generally do not act on carbon unless the carbon be heated, when the metals are reduced.

Red-hot carbon decomposes *ammonia*, forming ammonic cyanide, hydrogen, and nitrogen.

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Charcoal has certain remarkable physical and chemical properties of absorbing gases, &c., which we must consider.

(*a.*) *Its power of absorbing aqueous vapor.*—Recently ignited charcoal was found to absorb the following percentages, by weight, of *water*. (Allen and Pepys.)

	Weight of H_2O per cent. absorbed.
Lignum vitæ charcoal	9·6
Fir charcoal	13·0
Beech charcoal	16·0
Oak charcoal	16·5
Mahogany charcoal	18·0

(*b.*) *Its power of absorbing gases.*—A piece of *hard wood charcoal* was found to absorb gases in the following proportions:—

	Quantity of gas absorbed.
Ammonia (NH_3)	90 times its bulk.
Hydrochloric acid (HCl) ...	85 ,,
Sulphurous anhydride (SO_2)...	65 ,,
Sulphuretted hydrogen (H_2S)	55 ,,
Nitrous oxide (N_2O)	40 ,,
Carbonic acid (CO_2)	35 ,,
Carbonic oxide (CO)	9·4 ,,
Oxygen	9·2 ,,
Nitrogen	7·5 ,,
Hydrogen	1·75 ,,

Charcoal made from the shell of the cocoa-nut is said to be the most absorbent of all varieties.

(*c.*) *Its power of absorbing odors.*—The deodorizing property of charcoal is very marked. Hence its supposed antiseptic properties. It does not, however, prevent decomposition, but absorbs noxious gases and then oxidizes them by the oxygen condensed in its pores (Stenhouse), dissipating their carbon as carbonic acid, and their hydrogen as water. The ammonia formed is absorbed by the charcoal.

(*d.*) *Its power of absorbing coloring matters.*—The decolorizing property of charcoal is specially manifested in the case of *animal charcoal* or bone-black, possibly because it contains a large proportion of calcic phosphate, which serves to extend the carbon particles. Seaweed charcoal has also very considerable decolorizing power.

(*e.*) *Its power of absorbing mineral and other substances.*—Thus, if strychnia or iodine in solution, be shaken up with charcoal, they are rapidly absorbed. Lime may be abstracted from lime water, and lead acetate from its solutions by similar treatment. Charcoal is used by the distiller for the purpose of removing the empyreumatic oils from spirit.

Uses. (*a.*) *In nature.*—Carbon is found as a constituent of every organic substance. It gives the plant its solidity and its form.

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Hence organic chemistry has been defined as the chemistry of carbon and its compounds.

(*b.*) *In the arts.* (α.) *Diamonds* are used (1) as *gems;* (2) for *glass cutting;* and (3) for *lapidary work.* The diamond dust commonly used is the powder of the dark Brazilian diamond.

(β.) *Graphite* is used (1) for *pencils* (black lead); (2) for *black-leading* to protect iron from rust; (3) for *crucibles* mixed with clay (blue pots) on account of its power of resisting high temperatures and sudden changes; (4) as a *lubricator* to diminish the friction of machinery, and (5) as a facing for gunpowder as a *protectant.*

(γ.) *Lamp black,* owing to its unalterable nature, is used as a *pigment* in the manufacture of printing ink, blacking, etc.

(δ.) *Vegetable or wood charcoal* is used as a *disinfectant* and *deodorizer.* Thus, in *ventilating* sewers, in *covering graves,* in *dissecting rooms* and in hospital wards it is used to prevent offensive smells from putrescent matter, whilst in *respirators* it is employed to purify a vitiated air before it reaches the lungs.

(ε.) *Animal charcoal* is largely used as a *decolorizer* in sugar-refining, and in the purification of alkaloids, oils, etc.

(ζ.) *As an absorbent of impurities,* we employ animal charcoal for water filters, whilst in cases of poisoning by various substances, such as strychnia, etc., the injection of charcoal into the stomach as an absorbent, constitutes an important method of treatment.

(η.) *As a fuel* the use of charcoal is important. Coal is of vegetable origin, the change having been effected by a peculiar decomposition or fermentation, brought about by the agency of heat and moisture under great pressure, whereby much of the *hydrogen* of the wood is eliminated as marsh gas (CH_4), and the *oxygen* as carbonic anhydride (CO_2), the consequent accumulation of the carbon resulting. These changes are represented in successive steps as follows:—

	Carbon.	Hydrogen.	Oxygen.
(1.) Wood...	100	12·18	83·07
(2.) Peat	100	9·85	55·67
(3.) Lignite	100	8·37	42·42
(4.) Bituminous coal ...	100	6·12	21·23
(5.) Anthracite	100	2·84	1·74

The passage from wood to coal, therefore, consists in the storage of the carbon and in the elimination of the hydrogen and oxygen. A little sulphur is also present in coal, derived partly from vegetable albumen, and partly existing as FeS_2, derived from extraneous sources. There are also certain saline and earthy substances present, which constitute the coal ashes.

The composition of various kinds of coal is shown in the following table:—

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	Lignite.	Bituminous Coal.	Wigan Cannel.	Anthracite.	Coke.
Carbon	66·32	78·57	80·06	90·39	96·6
Hydrogen ..	5·63	5·29	5·53	3·28	0·4
Nitrogen	0·56	1·84	2·12	0·83	0·1
Oxygen	22·86	12·88	8·09	2·98	0·8
Sulphur	2·36	0·39	1·50	0·91	0·3
Ash	2·27	1·03	2·70	1·61	1·8
	100·00	100·00	100·00	100·00	100·0

The ash of coal varies, however, to a much greater extent than is stated above. A good coal should not contain more than 5 per cent. of ash, whilst a bad coal often contains 25 per cent. The following is the average percentage composition of 40 samples of ash:—

Silica	44·8
Lime	9·9
Magnesia...	2·4
Alumina and ferric oxide ...	33·7
Sulphuric acid	8·4
Phosphoric acid	0·8
	100·0

The *sulphur* present in the coal is important, the product of its combustion being sulphurous acid, a gas very destructive to vegetable life. Good coal should not contain more than from 1 to 1·5 per cent. of sulphur. The coke generally contains about one-half the quantity of the sulphur present in the coal from which it was prepared.

Amount of Sulphur in different varieties of Coal.

	Maximum.	Minimum.	Average.
Wales	5·07	0·09	36 exps. 1·47
Newcastle	2·85	0·06	18 ,, 1·24
Derbyshire ..	1·30	0·80	7 ,, 1·01
Lancashire ..	3·04	0·52	28 ,, 1·43
Scotland	1·57	0·33	8 ,, 1·11

When coal is heated *in close vessels*, the volatile ingredients, as well as the hydrogen, oxygen, and nitrogen present in the coal, are driven off, either in a free state or combined with more or less carbon, whilst coke (that is, carbon and earthy matters) remain in the retort. The composition of coke will be seen in the above table. The more intense the heat to which the coal is subjected, the more dense and the more incombustible the coke, and the better fitted it becomes for producing a steady and intense heat.

Process of burning coal in the open fire.—When the coal is heated it first softens, then swells up, and finally gives off certain gaseous pro-

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ducts (such as CH_4 and C_2H_4), which take fire. If sufficient oxygen was present, all the carbon would be dissipated as CO_2, and all the hydrogen as H_2O. This, however, never happens in a fire grate. Such gases as CH_4 and C_2H_4 (marsh and olefiant gases) burn without smoke, whilst a large quantity of hydrocarbons, such as benzol, naphthalene, etc., which are also formed, catch fire, but the oxygen being present in insufficient quantity, they undergo only partial combustion. The unconsumed carbon from these, together with ammonic carbonate and other products, escape to form the *smoke* and *soot*. The hot coke now left in the grate burns away until all the carbon is consumed, and the ash or incombustible mineral matter only remains.

When coke is used as a fuel, it does not undergo the first changes just described. Coke does not swell or soften, and for this reason cannot choke the draught like coal; and it is less combustible than coal, from the absence of inflammable hydrocarbons, and consequently burns without smoke.

It will be noted that *anthracite* or *steam coal* (stone coal or Welsh coal), contains more carbon and less hydrogen than ordinary coal. It, in fact, more nearly approaches the condition of coke. It therefore emits, when burnt, but little smoke and but little volatile matter, and consequently but little flame. Its principal use is for furnaces.

Smoke nuisances.—To remedy or reduce to a minimum the escape of smoke, three things are necessary:

1st. That the fuel should be supplied in small quantities at a time, and be placed well in front of the fire. (In Jucke's patent a regular supply of fuel is effected by mechanical means).

2nd. That a strong fire should be constantly maintained.

The fuel should be supplied in *small quantities*, in order that the volatile hydrocarbons should not be evolved in too great abundance at a time; and it should be put *in front of the fire*, so that before their escape they may pass over a large surface of glowing embers, whilst it is important that the *fire should be burning briskly*, in order that the gases and vapours may be consumed as fast as they are generated.

3rdly. There should be an adequate supply of air. In certain smoke preventers (as Hill's patent) hot air is supplied to the gases as they leave the fire, in order to complete the combustion of any unburnt portions.

It is clear that the prevention of smoke depends largely on the attention of the stoker.

Charcoal is often used as fuel. Its advantage over wood is twofold; (1.) That the moisture and volatile matters of the wood have been got rid of; and (2) that the percentage quantity of carbon is much greater in the charcoal than in the wood. In the first case much heat is lost when wood is used for fuel, in the formation of steam and volatile compounds, which is avoided by using charcoal; and in the second case, given weights of wood and charcoal being taken, the

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charcoal emits twice as much heat as wood. Thus the use of charcoal prevents loss and also concentrates heat.

(*c.*) In *medicine* charcoal has been employed in cases of dyspepsia, obstinate constipation, and as an application to foul ulcers, carbo animalis, B.P. (bone-black). The charcoal is purified (carbo animalis purificatus, B.P.) by digesting the crude charcoal in hydrochloric acid and water to remove the calcic phosphate. Carbo ligni, B.P., (wood charcoal,) is also officinal. It is often administered in the form of biscuits or lozenges. Its use in various cases of poisoning has been already noticed.

COMPOUNDS OF CARBON AND OXYGEN.

Carbonic oxide	CO.
Carbonic anhydride	CO_2.

Carbonic Oxide, CO (CO).

Molecular weight, 28. *Molecular volume*, |_|_|. *Relative weight*, 14. *Specific gravity*, 0·967.

Synomyms.—*Carbon monoxide.*

History.—Discovered by Priestley when igniting chalk in a gun barrel. He supposed it to be hydrogen. Its true nature was afterwards determined (1803) by Cruickshank, Clement, and Desormes.

Natural History.—It is never found except as an artificial product, as *e.g.* (1.) In the neighbourhood of *brick* or *lime kilns.* (2.) In the gases issuing from *iron blast-furnaces* (25 to 32 per cent.), from *copper refining furnaces* (15 per cent.), as well as from ordinary stoves. Its escape means waste.

Preparation.—(1.) By burning carbon in a limited supply of air.

(2.) By passing carbonic anhydride over red-hot iron. (Priestley.)

$$4CO_2 + Fe_3 = Fe_3O_4 + 4CO.$$

Carbonic anhydride + Iron = Magnetic oxide of iron + Carbonic oxide.

$$[4\mathbf{C}O_2 + Fe_3 = {}^{IV}(\mathbf{Fe})^{VIII}{}_3O_4 + 4CO].$$

(3.) By passing carbonic anhydride over red-hot carbon—

$$CO_2 + C = 2CO.$$

(4.) By acting on oxalic acid, or upon an oxalate with sulphuric acid.

$$C_2H_2O_4 + H_2SO_4 = CO_2 + CO + H_2O + H_2SO_4.$$

Oxalic acid + Sulphuric acid = Carbonic anhydride + Carbonic oxide + Water + Sulphuric acid.

$$\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right. + \mathbf{S}O_2Ho_2 = \mathbf{C}O_2 + \mathbf{C}O + \mathbf{O}H_2 + \mathbf{S}O_2Ho_2.$$

[NOTE.—(1.) The sulphuric acid merely abstracts water from the oxalic acid.

(2.) By washing the gaseous products with a solution of sodic hydrate, the CO_2 will be dissolved and the CO be left].

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(5.) By heating potassic ferrocyanide with sulphuric acid.

$K_4FeC_6N_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3N_2H_8SO_4 + 6CO.$

Potassic ferrocyanide + Sulphuric acid + Water = Potassic sulphate + Ferrous sulphate + Ammonic sulphate + Carbonic oxide.

$Fe''C_6N_6K_4 + 6SO_2Ho_2 + 6H_2O = 2SO_2Ko_2 + SO_2Feo'' + 3SO_2(NH_4O)_2 + 6CO.$

(6.) By heating a formate or formic acid with sulphuric acid.

$CH_2O_2 = H_2O + CO.$

Formic acid = Water + Carbonic oxide.

$\left[\begin{cases} H \\ COHo \end{cases} = OH_2 + CO. \right]$

Properties.—(α.) *Sensible.*—A colorless gas without odor or taste.

(β.) *Physiological.*—Carbonic oxide is a pure narcotic poison. Its effects were described by Guyton Morveau in 1802, and by Sir H. Davy in 1810. Its injurious effects, when injected into the veins, were discovered by Nysten. Tourdes proved that 1 part of the gas in 7 of air killed rabbits in seven minutes, 1 in 15 in twenty-three minutes, and 1 in 30 in thirty-seven minutes. Leblanc and Dumas' experiments show that air containing 1 per cent. of the gas will kill a dog in one and a-half minutes, and that birds die instantly in an atmosphere containing 5 per cent.

Dr. Letheby found in his experiments that air containing 0·5 per cent. of the gas, kills small birds in about three minutes, whilst an atmosphere containing 1 per cent. proves fatal in about half the time.

It has been held that the poisonous action of carbonic oxide depends on the formation in the blood of a new and fixed compound of carbonic oxide and hæmoglobin.

(γ.) *Physical.*—Its specific gravity is 0·972; the gas, therefore, is fourteen times heavier than hydrogen. It has never been condensed. It is decomposed, when passed through a red-hot tube, into carbon and carbonic anhydride. (*See* page 13.)

(δ.) *Chemical.*—Carbonic oxide is an indifferent oxide, and has no action either on litmus or turmeric. It burns with a pale blue and very hot flame, carbonic anhydride being the only product. It neither supports combustion, nor whitens lime water. It explodes with half its volume of oxygen, forming carbonic anhydride. It has no action on the metals, except on potassium, which absorbs it when heated ($K_2C_2O_2$). It combines with chlorine in sunlight to form phosgene gas ($COCl_2$). It is slightly soluble in water, 100 volumes dissolving 2·43 volumes at 60° F. It forms potassic formate when heated with potassic hydrate ($KHO + CO = CHKO_2$). It is absorbed by a solution of cuprous chloride in hydrochloric acid, forming the compound $CO,Cu_2Cl_2 2H_2O$. On boiling this liquid, the gas is expelled unaltered.

The carbonic oxide flame is employed in the reverberatory furnace, where it is made to play over metallic ores, thereby reducing them, the CO forming CO_2 at the expense of the oxygen of the metallic oxide.

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The carbonic oxide is produced by causing the carbonic anhydride formed at the bottom of the grate to pass through the hot coal in the grate ($CO_2+C=2CO$). The same thing occurs in an ordinary stove, the CO_2 formed at the bottom of the stove, where there is plenty of air, becoming CO as it passes through the fire, which burns as soon as it reaches the surface. Carbonic oxide is present to the extent of 34 per cent. in water gas. This is prepared by first passing steam over red-hot coke, whereby hydrogen and carbonic oxide are formed ($4H_2O+C_3=CO_2+2CO+4H_2$), and afterwards supplying the combustible gases with illuminating properties, by causing them to traverse red-hot coke saturated with melted resin. The presence of so large a quantity of carbonic oxide would render the use of water gas very dangerous. Common coal gas also contains from 4 to 7 per cent. of carbonic oxide.

Carbonic Anhydride, ($CO_2=44$) ($\mathbf{C}O_2$).

Molecular weight, 44. *Molecular volume*, |_|_|. *Relative weight*, 22. *Specific gravity*, 1·529. 100 *cubic inches weigh* 47·445 *grains, and* 1 *litre* 1·9774 *grms.*

Synonyms.—Commonly called *Carbonic acid; Carbon or Carbonic Dioxide; Mephitic Air; Gas Sylvestre; Fixed Air* (Black); *Choke Damp.*

History.—Carbonic anhydride was known to Paracelsus and Von Helmont. It was examined by Black in 1757, and called by him 'Fixed Air.' In 1775 Lavoisier, by careful experiments on the products of the combustion of the diamond, determined its exact nature and named it carbonic acid.

Natural History. (α.) *In the mineral kingdom* carbonic anhydride is found *free* in the air. It is evolved—

(1.) *As a product of respiration in man and animals.*—Respired air contains about 4 per cent. of carbonic anhydride.

(2.) *As a product of fermentation.*—Thus, accidents have arisen from plunging the head into fermenting vats.

(3.) *As a product of lime burning.*—Calcic carbonate when heated evolves carbonic anhydride, leaving caustic lime ($CaCO_3=CaO+CO_2$). By subterranean heat in volcanic districts a similar action takes place; thus immense quantities of CO_2 are given out into the air, whilst the springs in the neighbourhood become charged with the gas.

(4.) *As a product of slow oxidation.*—Thus, spring water becomes impregnated with carbonic acid, from the oxidation of the organic matter by the oxygen dissolved in the water. If a bottle half full of water containing organic matter, be kept in a warm room and in a closed vessel, the oxygen in the bottle will be found after a time to be more or less completely replaced by a corresponding volume of carbonic anhydride. So also carbonic anhydride is found in old wells and cellars, where it is produced by the decay of organic matter and in some cases, perhaps, exhaled from the earth.

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(5.) *As a product of the explosion of fire-damp, or carburetted hydrogen.*—The product of the explosion (*choke damp*) is more often the cause of deaths than even the explosion itself.

(6.) *As a product of combustion.*—All bodies containing carbon yield by combustion carbonic anhydride. Two ordinary candles produce as much carbonic anhydride in an equal time as one adult (Angus Smith).

It is also found in a combined state in carbonates, as in limestone, marble, and chalk.

(β.) It is not found in any great quantity in the *vegetable kingdom*, the special action of the plant being to decompose it, whilst (γ) in *the animal kingdom* it is found in the exhaled air derived from the combustion of tissue.

Preparation. (1.) By burning carbon in air or oxygen ($C+O_2=CO_2$).

(2.) By the action of acids on carbonates. If sulphuric acid be poured on marble, carbonic anhydride is set free, but the action is soon arrested by the formation of an insoluble sulphate over the surface of the marble. Hence we ordinarily employ HCl for the purpose :—

$CaCO_3$	+	$2HCl$	=	$CaCl_2$	+	H_2O	+	CO_2
Calcic carbonate	+	Hydrochloric acid	=	Calcic chloride	+	Water	+	Carbonic anhydride.
[COCao″	+	$2HCl$	=	$CaCl_2$	+	OH_2	+	CO_2].

It must be collected by displacement.

Properties.—(α.) *Sensible.* Carbonic anhydride is a colorless gas. It has no odor when largely diluted with air, but the presence of above 5 per cent. of CO_2 renders the air irritating and pungent.

(β.) *Physiological.* When *swallowed*, the gas is harmless. *Inhaled*, it acts as a narcotic poison.

(1.) The *undiluted* gas kills instantly by spasm of the glottis.

(2.) When *diluted* with air, so that the proportion of the gas present is about 12 or 14 per cent. (as in a room where a chafing dish has been burnt) it causes giddiness, hurried circulation, fulness in the head, noises, confusion, perhaps delirium, and finally coma, which may last a considerable time.

(3.) Air containing 4 or 5 per cent. of carbonic anhydride (such as air once breathed) causes a sense of oppression with headache, distress, and perhaps delirium or coma.

(4.) Air containing 3 per cent. of carbonic anhydride cannot be breathed without great distress, and will probably produce insensibility.

(5.) An atmosphere containing 1 or even 0·5 per cent. of carbonic anhydride (such as is found in ill-ventilated theatres) is distressing.

(6.) Its presence in the proportion of 0·1 per cent. may be considered the boundary line between good and bad air.

These facts show the necessity of good ventilation. Although

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carbonic anhydride is half as heavy again as air, nevertheless the processes whereby it is produced by raising its temperature render it specifically lighter. Thus it *ascends* and accumulates near the ceiling. The chimney opening only ventilates the lower part of the room.

(γ.) *Physical.* The specific gravity of carbonic anhydride is 1·529, that is, it is 22 times heavier than hydrogen; 100 cubic inches weigh 47·445 grains, and 1 litre 1·9774 grm. Hence it accumulates on the floors of caves and caverns (Grotto del Cane). By a pressure of 50 atmospheres at 59° F. (15° C.), or by a pressure of 38·5 atmospheres at 32° F. (0° C.), the gas may be liquefied, the liquid having a gravity of 0·83. It is important to note here, that in liquefying gases by cold and pressure, an *increased pressure* is not necessarily equivalent to a *reduced temperature.* For in every liquefiable gas there is a temperature at which it cannot be liquefied by any attainable pressure. This is termed the "*critical point,*" that is, the point where the gas is wavering between the gaseous and the liquid state. Thus, if you heat carbonic anhydride to 88° F. (31·1° C.), no known pressure (109 atmospheres having been tried) will effect its liquefaction.

Liquid carbonic anhydride does not mix freely with water, but is soluble in spirit, ether, turpentine, carbonic disulphide, etc. If the liquid be cooled to —70° F. (—56° C.), or if it be allowed to escape into the air, it instantly freezes into a snow-white solid, the cold produced by its evaporation in the latter case answering to the artificial cold in the former. It evaporates without melting, inasmuch as the heat it requires for its evaporation keeps it as low as —125° F. (—87·2° C.), whilst it melts at —85° F. (—65° C.). It conducts electricity badly. The greatest known cold (—148° F., or —100° C.), is produced by the evaporation of a mixture of solid carbonic anhydride and ether "*in vacuo.*"

A heat of 2192° F. (1200° C.) decomposes carbonic anhydride into oxygen and carbonic oxide, re-combination occurring if the mixture be allowed to cool slowly. Similarly, the heat of the electric spark will affect dissociation, the oxygen set free being said to be in an ozonised condition.

At ordinary pressure, 1 volume of water absorbs 1 volume of the gas; at 2 pressures, 2 volumes; at 3 pressures, 3 volumes, etc.; but on the removal of the extra pressure all the dissolved gas escapes except the original volume. Thus, by pressure under the earth, water may be made to take up an extra quantity of gas, whereby it is rendered effervescent when it comes to the surface.

The rain as it falls dissolves atmospheric carbonic anhydride. This solution acts on certain rocks, slowly crumbling and disintegrating them. This process of rock disintegration is assisted by the expansion of the water in the interstices of the rock during congelation. Thus soils are formed of the broken down *débris* ($Na_4SiO_4 + 4H_2O + 4CO_2 = H_4SiO_4 + 4NaHCO_3$). Further, owing to the solubility of the

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gas in water, the rain brings it to the roots of plants, the solution dissolving the calcic phosphate which is insoluble in pure water.

(δ.) *Chemical.*—The gaseous, but not the liquid carbonic anhydride, effects a transient reddening of blue litmus. The pure gas instantly extinguishes a flame. We may classify the results of dilute carbonic anhydride as follows:—

An atmosphere containing	Action on flame.
16 per cent. of CO_2.	Flame instantly extinguished.
12 ,, ,,	Flame extinguished if not burning vigorously.
10 ,, ,,	Taper burns, but the flame considerably dulled.
8 ,, ,,	Taper burns readily.

Thus it is evident that a taper may burn in an atmosphere that is dangerous and even fatal to life.

Potassium burns in carbonic anhydride, setting free carbon ($3CO_2 + 2K_2 = 2K_2CO_3 + C$). Sodic oxalate is formed when the gas is passed into melted sodium ($2CO_2 + Na_2 = C_2Na_2O_4$), and potassic formate, together with hydric potassic carbonate, when the moist gas is brought into contact with potassium ($2CO_2 + K_2 + H_2O = KHCO_2 + KHCO_3$).

Carbonic acid (H_2CO_3) is not known.

Tests.—A white precipitate with lime or baryta water. Its ready solubility in a solution of potassic hydrate enables us to separate it from most other gases.

Compounds of Carbon and the Haloids.

Compounds of Carbon and Chlorine.

Carbonic Tetrachloride	CCl_4.
Carbonic Trichloride	C_2Cl_6.
Carbonic Dichloride	C_2Cl_4.
Carbonic Monochloride	C_2Cl_2, or C_6Cl_6.

These compounds are all prepared by indirect methods.

Carbonic Tetrachloride ($CCl_4 = 154$).

Synonym.—*Bichloride of carbon.*

History.—Discovered by Regnault.

Preparation.—(1.) By the action of chlorine on marsh gas (CH_4).

(2.) By passing chlorine and carbonic disulphide vapor through a red-hot tube ($CS_2 + 4Cl_2 = CCl_4 + 2SCl_2$). The sulphur chloride may be dissolved out by a solution of potassic hydrate.

Properties.—A colorless liquid. Specific gravity, 1·56. Boils at 172° F. (77° C.); freezes at —9° F. (—22·8° C.). It is insoluble in water, but is soluble in alcohol, and in ether. It freely dissolves fats, resins, etc. By the action upon it of zinc and hydrochloric acid, chloroform may be obtained. Its vapor is powerfully anæsthetic.

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Carbonic Trichloride (C_2Cl_6=202).

Synonym.—*Sesquichloride of carbon.*

History.—Discovered by Faraday.

Preparation.—(1.) By the action of sunlight on a mixture of Dutch liquid ($C_2H_4Cl_2$) and chlorine ($C_2H_4Cl_2+4Cl_2=C_2Cl_6+4HCl$).

(2.) By passing the vapor of carbonic tetrachloride (CCl_4) through a red-hot tube.

Properties.—A white crystalline solid, having an aromatic camphory odor. It fuses at 320° F. (160° C.), and boils at 360° F. (182·2° C.), when it sublimes unchanged. It is volatile at ordinary temperatures. It is insoluble in water, but is soluble in ether and in alcohol.

Carbonic Dichloride (C_2Cl_4=164).

Synonym.—*Protochloride of carbon.*

History.—Discovered by Faraday.

Preparation.—(1.) By passing the vapors of CCl_4 or C_2Cl_6 through a red-hot tube.

(2.) By the action of nascent hydrogen on carbonic trichloride (C_2Cl_6).

Properties.—A liquid. Specific gravity, 1·19. Boils at 248° F. (117° C.). It is insoluble in water, but is soluble in alcohol, and in ether.

Carbonic Monochloride, C_2Cl_2, or C_6Cl_6.

Synonyms.—*Carbonic subchloride* or *Hexachloride.*

Preparation.—(1.) By passing either the vapor of C_2Cl_4 or of chloroform through a red-hot tube.

(2.) By the action of chlorine on benzene.

Properties.—A white crystalline solid without odor, insoluble in water, but soluble in ether and hot alcohol. It melts at 438·8° F. (226° C.), and boils, subliming unchanged at 627·8° F. (331° C.).

Compounds of Carbon with Bromine, Etc.

A *carbonic tetrabromide* (CBr_4); a *carbonic tribromide* (C_2Br_6), prepared by acting on C_2Br_4 with bromine; and a *carbonic dibromide* (C_2Br_4) prepared by acting on ether or alcohol with bromine, all three of which are white crystalline bodies, have been described.

By the action of bromine in sunlight on carbonic dichloride (C_2Cl_4), a *carbonic chlorobromide* ($C_2Cl_4Br_2$), a crystalline body, is formed.

No compound of carbon and iodine has been for certain discovered.

Compounds of Carbon with Oxygen and the Haloids.

Carbonic Oxychloride, $COCl_2$.

Synonyms.—*Chlorocarbonic acid; Carbonyl chloride; Phosgene gas.*

Preparation.—(1.) By exposing equal volumes of carbonic oxide

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and chlorine to sunlight, the mixture condensing to one-half its original volume.

(2.) By heating together carbonic tetrachloride and zincic oxide ($2CCl_4 + 3ZnO = 3ZnCl_2 + COCl_2 + CO_2$).

(3.) By the oxidation of chloroform.

Properties.—A colorless pungent gas. It is decomposed by water. For this reason it fumes in the air, the chlorine combining with the hydrogen of the moisture ($COCl_2 + H_2O = CO_2 + 2HCl$). By a cold of 5° F. (—15° C.), it forms a liquid which has a specific gravity of 1·432 at 32° F. (0° C.), and boils at 46·3° F. (8·2° C.).

With ammonia it forms urea and ammonic chloride.

$$4NH_3 + COCl_2 = COH_4N_2 + 2NH_4Cl.$$

Ammonia + Phosgene gas = Urea + Ammonic chloride.

This reaction illustrates the property of phosgene gas in effecting the displacement of hydrogen and its substitution by carbonic oxide.

The analogous bromine and iodine compounds have not been prepared.

Compounds of Carbon and Sulphur.

Carbonic Disulphide (CS_2).

Synonyms.—*Bisulphuret* or *Bisulphide of carbon; Sulphocarbonic acid.*

History.—Discovered accidentally by Lampadius in 1796 whilst distilling iron pyrites.

Preparation.—(1.) By passing the vapor of sulphur over heated charcoal ($C + S_2 = CS_2$).

(2.) By heating together charcoal and iron, or charcoal and copper pyrites ($C + 2FeS_2 = CS_2 + 2FeS$).

Properties.—(*a.*) *Sensible.*—An ethereal colorless liquid having a peculiar odor.

(*β.*) *Physiological.*—Its action is anæsthetic, and in excess it acts as a poison. It is used for destroying insects in grain.

(*γ.*) *Physical.*—Specific gravity of liquid, 1·272; of vapor, 2·63. It boils at 110° F. (43·3° C.), but it cannot be frozen. It refracts light powerfully. It is volatile at ordinary temperatures.

(*δ.*) *Chemical.*—It has no action on litmus. It fires at 360° F. (182·2° C.), the products of its combustion being CO_2 and SO_2. It explodes vehemently when mixed with oxygen. Potassium burns in the vapor with the liberation of carbon, and the formation of a potassic sulphide ($CS_2 + 2K_2 = 2SK_2 + C$). When the vapor is passed over many red-hot metallic oxides, it changes them into sulphides. When a mixture of the vapor and sulphuretted hydrogen is passed over hot copper, it yields a sulphide of copper and marsh gas ($CS_2 + 2H_2S + Cu_8 = 4Cu_2S + CH_4$).

It combines with alkaline hydrates, and with alkaline sulphides to form *sulphocarbonates* ($M''CS_3$), which are bodies analogous to the carbonates, but containing sulphur in the place of oxygen ($CaCO_3$

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—$CaCS_3$). When the sulphocarbonates are boiled with water they become carbonates. *Sulphocarbonic acid* (H_2CS_3) may be prepared by the action of hydrochloric acid on the salts. It is a yellow oily liquid.

Carbonic disulphide is nearly insoluble in water, but very soluble in alcohol and in ether. It is a solvent, moreover, of many bodies, such as sulphur, phosphorus, iodine, the alkaloids, oils, gums, resins, fats, etc. Hence its use. It is also employed in making thermometers for registering very low temperatures.

It forms one of the most troublesome impurities of coal gas.

Carbonic Oxysulphide (COS).

This body, which was discovered by Thau, may be regarded as H_2S, where $(CO)''$ has replaced the H_2.

Preparation.—(1.) By heating a mixture of sulphur vapor and carbonic oxide.

(2.) By heating together potassic sulphocyanide and dilute sulphuric acid. A hydrosulphocyanic acid is first formed ($KCNS + H_2SO_4 = HCNS + KHSO_4$) and afterwards decomposed by the water into carbonic oxysulphide and ammonia, the latter being absorbed by the excess of acid ($HCNS + H_2O = NH_3 + COS$).

(3.) By heating a mixture of urea and carbonic disulphide.

Properties.—A combustible, aromatic gas, decomposed by heat into CO and S. It is slightly soluble in water, the solution decomposing after a time spontaneously (or immediately if an alkali be present), into carbonic anhydride and sulphuretted hydrogen. It has no action upon an acid solution of lead, copper or silver.

BORON (B=11).

Atomic weight, 11. *Molecular weight (probable)*, 22. *Triad* (BCl_3—BF_3.)

History.—Prepared by Davy (1807), by the action of the galvanic current on boracic acid. Guy Lussac and Thénard (1808) prepared it by acting on boric anhydride with potassium. Wohler and Deville (1857) first prepared the crystalline modification.

Natural History.—It is never found in nature in a free state. It occurs as boracic acid in the lagoons of Tuscany, and in combination with *soda* as tincal, with *magnesia* as boracite, and with *lime* as boracalcite, etc.

Varieties.—Three varieties have been described, viz., the *amorphous*, the *graphoidal*, and the *crystalline*. The graphoidal modification, however, is probably a compound of AlB_2.

Preparation.—(a.) *Amorphous boron.*

(1.) By fusing together boric oxide and sodium ($B_2O_3 + 3Na_2 = 3Na_2O + B_2$).

(2.) By the action of boric oxide on potassium, or on potassic borofluoride.

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(β.) *Crystalline* (*diamond*) *boron.*

By fusing together boric oxide and aluminium ($B_2O_3 + Al_2 = Al_2O_3 + B_2$).

Properties.—The *amorphous* modification of boron is an olive-green powder, and burns both in oxygen (forming B_2O_3) and in chlorine (forming BCl_3). It is insoluble in water. When burnt in air, a trace of boric nitride (BN) is formed. It decomposes hot *sulphuric acid* ($3H_2SO_4 + B_2 = B_2O_3 + 3H_2O + 3SO_2$), and *nitric acid* It also decomposes the alkaline *carbonates*, *sulphates*, and *nitrates*, setting free carbonic oxide, sulphurous anhydride, and nitric peroxide respectively.

Crystalline or *diamond boron* (adamantine boron) which, next to the diamond, is the hardest substance known, has a specific gravity of 2·68, and when pure is colorless, and a powerful optical refractor. It is infusible, and is not acted upon by strong acids, but it burns when heated to redness in chlorine. It forms boric oxide when fused with potassic sulphate ($6KHSO_4 + B_2 = B_2O_3 + 3K_2SO_4 + 3H_2O + 3SO_2$).

[Boric or Boracic Acid (H_3BO_3 or BHo_3). Boracic Anhydride (B_2O_3)].

Preparation and Natural History.—The acid was originally prepared by Homberg (1702) and by Lemery (1727) by the action either of dilute sulphuric acid, as suggested by the latter, or of dehydrated ferrous sulphate, as suggested by the former, on borax ($Na_2O, 2B_2O_3 + 10aq$ called *Sedative Salt*, and, when in the rough, *Tincal*).

The acid is now obtained as follows:—In certain volcanic districts boracic acid is discharged from the earth in a free and vaporous state, accompanied by steam jets (suffioni). We know nothing of its actual origin. For the purpose of condensing these steam jets, brick basins (lagoons) are erected at the site of the discharge, and are filled with water from neighbouring springs. A series of these lagoons is constructed in a descending line, so that the water may flow from one to the other. The acid solution which collects in the basins is then evaporated down in leaden pans, the suffioni themselves being employed as the source of heat. The acid is then purified by crystallization.

Properties. (α.) *Physical.*—The acid has a bitter taste and crystallizes in scales. At 248° F. (120° C.) it becomes HBO_2 or $BOHo$ (*meta-boric acid*). At a higher temperature a hygroscopic body (B_2O_3) is formed, which at a greater heat fuses to a clear glass (*vitreous boric acid*) which finally volatilizes.

It is soluble in 3 parts by weight of boiling water and in 26 parts of cold, but its solubility is irregular. It is soluble in spirit, the solution burning with a green flame.

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(β.) *Chemical.*—The solution of the acid is faintly acid to litmus, but if a piece of turmeric paper be dipped into the solution and dried, it becomes of a brown red color. If this be moistened with an alkali it changes to an intense blue.

The acid forms salts called borates.

Boric Nitride, BN or B_3N_3.

Preparation.—By heating boron in nitrogen, in air, or in ammonia gas, or by heating a mixture either of boric oxide and urea, or of borax and ammonic chloride.

Properties.—A white, infusible, and insoluble powder.

A *boric chloride* (BCl_3), a liquid prepared by burning boron in chlorine; a *boric bromide* (BBr_3), a liquid also prepared by direct union; a *boric fluoride* (BF_3), a gas prepared by heating a mixture of borax, fluor spar, and sulphuric acid, have been described. Moreover, a *boric sulphide* (B_2S_3), a white solid, formed by direct union, is known.

A *fluoboric* acid ($HBO_2 3HF$) and a *hydrofluoboric* acid (HBF_4) formed by the action of water on boric fluoride are also known.

SILICON or SILICIUM (Si=28·5).

Atomicity, tetrad, as in $SiCl_4$.

History.—Silicon was discovered by Davy (1807), when acting on silicic acid with potassium. Berzelius (1824) obtained it by the action of potassium on fluosilicic acid.

Natural History.—Silicon has never been found in a free state. It occurs (α.), in the *mineral* kingdom, as silica (SiO_2); both in a *crystallized* form, as quartz; and in a *non-crystallized* form, as flint, chalcedony, opal, etc. It also exists abundantly in combination with metallic oxides. Clays are aluminic silicates. (β.) In the *vegetable* kingdom it is found in the stems of cereals; (γ) and in the *animal* kingdom in teeth, feathers, bones, etc.

Varieties.—Silicon exists in three modifications; (α) *amorphous;* (β) *graphoidal;* and (γ) *crystalline.*

Preparation.—(α.) *Amorphous Silicon.*

(1.) By heating together potassium and potassic-silico-fluoride (fluoride of silicon and potassium).

$$SiK_2F_6 + 2K_2 = 6KF + Si.$$

Potassic silico-fluoride + Potassium = Potassic fluoride + Silicon.

(2.) By heating sodium in the vapor of silicic chloride ($SiCl_4 + 2Na_2 = Si + 4NaCl$).

(β.) *Graphoidal Silicon.*—By fusing together aluminium and amorphous silicon, and afterwards dissolving out the aluminium from the mixture by boiling hydrochloric acid.

(γ.) *Adamantine Silicon.*

(1.) By fusing amorphous silicon.

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(2.) By heating aluminium in a current of silicic chloride vapor ($3SiCl_4 + 2Al_2 = 2Al_2Cl_6 + 3Si$).

Properties.—(α.) *Of amorphous silicon.* A dark brown powder. Specific gravity 2·0. Infusible and involatile. It neither conducts heat nor electricity. It burns when heated in air or oxygen, forming SiO_2. It is not acted on by any solvents except hydrofluoric acid (fluorine having a great affinity for silicon), forming hydrofluosilicic acid ($Si + 6HF = SiH_2F_6 + 2H_2$). When fused with potassic hydrate, hydrogen is evolved, and a potassic silicate formed ($Si + 4KHO = K_4SiO_4 + 2H_2$). By fusion with aluminium the graphoidal modification is produced.

(β.) *Of graphoidal silicon.* It is found in the form of crystalline metallic-looking scales, having a specific gravity of 2·49. It conducts electricity. It does not burn in oxygen. It is not dissolved by hydrofluoric acid, but is soluble in a mixture of hydrofluoric and nitric acids. It is slowly acted upon when fused with potassic hydrate.

(γ.) *Of adamantine silicon.*—Adamantine silicon is even less prone to oxidation than the graphoidal modification. It resembles crystallized hæmatite both in color and appearance.

Compounds of Silicon and Oxygen.

Silica ($SiO_2 = 60$) (SiO_2).

Synonyms.—*Silicon dioxide; Silicic anhydride.*

Natural History.—Silica occurs, in the mineral kingdom, both in a crystalline and in an amorphous form. *Quartz* (*i. e.*, rock crystal, consisting of six-sided crystals terminated by six-sided pyramids), *Amethyst* (the purple color of which is due to iron), *Cairngorm* (a yellow or brown stone), are illustrations of the crystalline variety; and *Agate*, *Chalcedony* (which in layers of different colors constitutes *Onyx*), *Jasper*, *Cornelian* (the color of which is due to ferric oxide), *Flint*, and *Opal* (where the silica is combined with varying quantities of water), are illustrations of the amorphous variety.

Sand is very nearly pure silica, its different colors depending on the presence of various foreign matters. It forms the chief support of the soil. Plants absorb it freely, as shown by its presence in the stems of rushes and cereals. This, and its presence in solution in certain natural waters, as in the Geysers, prove the possibility of its existing in a soluble form.

All the artificial forms of silica are of the amorphous modification.

Properties.—Pure silica, when *en masse*, is a hard, colorless, transparent body, but when finely powdered appears white. The *crystalline* form has a specific gravity of 2·7, and the amorphous of 2·2. Both forms are non-volatile, but by oxy-hydrogen heat they fuse to a clear glass, the crystalline thereby becoming the amorphous modification. They are insoluble in pure water, and in all acids except hydrofluoric.

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The amorphous form is soluble in solutions of the caustic alkalies, and is slightly soluble in the alkaline carbonates. By heating finely powdered quartz (but not if it be in lump), it is converted into the amorphous variety, and becomes soluble in alkalies.

The ordinary vegetable acids (as *e. g.* tartaric acid), or a weak acid (such as carbonic acid), precipitate silica from its solutions; nevertheless, *at a high temperature*, silica being *non-volatile*, decomposes carbonates and even sulphates.

Silica is soluble in fused borax, but not in microcosmic salt.

Silicic Acid.

H_4SiO_4, or $2H_2O,SiO_2$, or $\mathbf{Si}Ho_4$ (*tetrabasic acid*).
H_2SiO_3, or H_2O,SiO_2, or $\mathbf{Si}OHo_2$ (*dibasic acid*).

At the moment that silica is liberated from its soluble compounds, it is soluble in water, silicic acid being thereby formed. This is found in the two modifications mentioned above.

Preparation.—(1.) If silica be fused with sodic carbonate, carbonic acid escapes and a sodic silicate is formed. This salt is alkaline, and soluble in water. If a few drops of hydrochloric acid (*i. e., not sufficient to render it acid*) be added to its solution, it forms a gelatinous mass, from the separation of hydrated silicic acid. If an excess of acid, however, be added (*i. e., sufficient to render it acid*), silicic acid, together with sodic chloride, are produced, and both remain in solution:—

$$Na_4SiO_4 + 4HCl = H_4SiO_4 + 4NaCl.$$
Sodic silicate + Hydrochloric acid = Silicic acid + Sodic chloride.
$$[\mathbf{Si}Nao_4 + 4HCl = \mathbf{Si}Ho_4 + 4NaCl.$$

If this solution be dialysed, the sodic chloride, with any excess of hydrochloric acid, will pass through the dialyser, whilst a pure solution of silicic acid will remain on the dialyser.

Substances (like sodic chloride) that diffuse rapidly are termed *crystalloids*, and those having a low rate of diffusion (such as silicic acid) are termed *colloids*.

(2.) It may also be prepared by the action of carbonic anhydride on a solution of sodic or other soluble silicate. This action is similar to that which occurs in the natural disintegration of granite.

$$Na_4SiO_4 + 4H_2O + 4CO_2 = H_4SiO_4 + 4NaHCO_3.$$
Sodic silicate + Water + Carbonic anhydride = Silicic acid + Hydric sodic carbonate.
$$[\mathbf{Si}Nao_4 + 4\mathbf{O}H_2 + 4\mathbf{C}O_2 = \mathbf{Si}Ho_4 + 4\mathbf{C}OHoNao.]$$

(3.) By the action of water on silicic fluoride:—

$$3SiF_4 + 4H_2O = H_4SiO_4 + 2SiH_2F_6.$$
Silicic fluoride + Water = Silicic acid + Hydrofluosilicic acid.
$$[3\mathbf{Si}F_4 + 4\mathbf{O}H_2 = \mathbf{Si}Ho_4 + 2HF,\mathbf{Si}F_4.]$$

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Properties.—The solution of silicic acid may, by cautious evaporation, be concentrated until it contains 14 per cent. of the acid (H_4SiO_4). In this state it is a colorless tasteless liquid, and faintly acid to litmus. By keeping, the acid separates from the water as a gelatinous mass, which shrinks in drying, and when dry has the formula $Si_6H_8O_{16}$ ($\mathbf{Si}_6O_8Ho_8$). If this be heated to 212° F. (100° C.), it loses water and becomes $Si_6H_4O_{14}$ ($\mathbf{Si}_6O_{10}Ho_4$).

If the solution be evaporated *in vacuo* over sulphuric acid, a lustrous glass is formed, containing 78 per cent. of silicic acid (H_2O,SiO_2). This is insoluble in water, and but very slightly soluble in hydrochloric acid. By further heat the anhydrous acid may be obtained, which is insoluble both in hydrofluoric acid and in water, but is soluble in boiling solutions of the caustic alkalies.

Compounds of Silicon and the Haloids, Etc.

Compounds of Silicon and Chlorine.

Silicic tetrachloride	$SiCl_4$.
Silicic trichloride	Si_2Cl_6.
Silicic hydrotrichloride	$SiHCl_3$.

Silicic Tetrachloride ($SiCl_4$).

Synonym.—*Silicic Chloride.*

Preparation.—(1.) By burning silicon in chlorine.

(2.) By heating carbon and silicic anhydride in a stream of chlorine.

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$

Silicic anhydride + Carbon + Chlorine = Silicon tetrachloride + Carbonic oxide.

$$[\mathbf{Si}O_2 + 2C + 2Cl_2 = \mathbf{Si}Cl_4 + 2\mathbf{C}O].$$

Properties.—A transparent, pungent-smelling, colorless, very volatile liquid. It fumes in the air from the deposition of silica by the action of the moisture. The specific gravity of the liquid at 32° F. (0° C.), is 1·5237, and of the vapor 5·939. It boils at 138·2° F. (59° C.). Water decomposes it into hydrochloric and silicic acids ($SiCl_4+4\mathbf{O}H_2=\mathbf{Si}Ho_4+4HCl$).

Silicic Trichloride (Si_2Cl_3), formed by acting on silicon with carbon tetrachloride, has been prepared. It is a colorless liquid (Sp. Gr. 1·58). Its vapor is spontaneously inflammable.

Silicic Hydrotrichloride.—($SiHCl_3$) (*Silicon chloroform*), is prepared by heating crystallized silicon in a stream of hydrochloric acid ($Si+3HCl=SiHCl_3+H_2$). It is a fuming liquid, boiling at 96·5° F. (36° C.). The vapor is very inflammable, and explodes when mixed with oxygen. It is decomposed either (1) by passing it through a red-hot tube, or (2), at ordinary temperatures by the action of chlorine, or, (3), by contact with water.

Several **Silicic oxychlorides** have been prepared.

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COMPOUNDS OF SILICON WITH BROMINE, IODINE, ETC.

Silicic Tetrabromide ($SiBr_4$) is prepared similarly to the chlorine compound. It is a colorless, heavy liquid, boiling at 307·4° F. (153° C.).

Silicic Tribromide (Si_2Br_6) is also a crystalline substance.

Silicic Tetriodide (SiI_4) is a crystalline body, prepared by passing iodine vapor and carbonic anhydride over heated silicon.

Silicic Triiodide (Si_2I_6) is also a crystalline solid, prepared by the action of metallic silver on SiI_4.

Silicic Iodoform ($SiHI_3$), corresponding to silicon chloroform, has been prepared by passing hydrogen and hydriodic acid over heated silicon. It is a liquid (Sp. Gr. 3·362), and is decomposed by water.

COMPOUNDS OF SILICON WITH FLUORINE, ETC.

Silicic Fluoride (SiF_4).

Synonym.—*Silicic Tetrafluoride.*

Preparation.—By heating together silica, calcic fluoride and sulphuric acid.

SiO_2	+	$2CaF_2$	+	$2H_2SO_4$	=	SiF_4	+	$2CaSO_4H_2O$.
Silica	+	Calcic fluoride	+	Sulphuric acid	=	Silicic fluoride	+	Dihydric calcic sulphate.
[**Si**O_2	+	2**Ca**F_2	+	2**S**O_2Ho_2	=	**Si**F_4	+	2**S**OHo_2Cao''].

Properties.—A heavy, colorless, fuming gas. Specific gravity 3·6. It neither burns nor supports combustion. It may be liquefied by pressure, and solidified by a cold of —220° F. (—140° C.). By the action of water upon it, silicic and fluosilicic acids are formed.

$3SiF_4$	+	$4H_2O$	=	H_4SiO_4	+	$2SiH_2F_6$.
Silicic fluoride	+	Water	=	Silicic acid	+	Hydrofluosilicic acid.
[3**Si**F_4	+	4**O**H_2	=	**Si**Ho_4	+	$2(2HF,$**Si**$F_4)$].

Many metallic oxides (as lime) absorb it freely.

Hydrofluosilicic Acid ($2HF,SiF_4$ or H_2SiF_6).

Synonym.—*Silico-fluoric acid.*

Preparation.—By the action of water on silicic fluoride. (*See* last equation.)

Properties.—The solution is a fuming acid liquid. It does not attack glass. When heated, silicic fluoride is evolved, and hydrofluoric acid, which readily dissolves glass, remains in solution.

Neutralised with bases, a hydro-fluosilicate is formed ($2KHO + 2HF,SiF_4 = 2H_2O + 2KF,SiF_4$); but if the base be added in excess,

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silica is thrown down, and a metallic fluoride produced ($6KHO + 2HF,SiF_4 = 4H_2O + 6KF + SiO_2$). The baric and potassic hydrofluosilicates are very insoluble.

Silicic Nitride (Formula ?) is formed by the direct combination of silica and nitrogen, at a high temperature. It is a white infusible body, soluble only in hydrofluoric acid, forming ammonic silicofluoride. When heated in carbonic anhydride, it forms ammonic carbonate. When heated in steam, ammonia is set free. It is not acted upon by chlorine, nor does heat alone affect it.

Silicic Sulphide (SiS_2) (*bisulphide of silicon*), is prepared either by direct union, or by passing CS_2 vapor over a mixture of charcoal and silica. It is a white amorphous hygroscopic solid, soluble in water, by which it is decomposed into silica and hydro-sulphuric acid ($SiS_2 + 2H_2O = SiO_2 + 2H_2S$).

Silico-Formic Acid, or **Leukon** (λευκὸς white) (SiH_2O_2) (*silicon formanhydride*) is formed by the action of water on silicon chloroform. It is a white substance, decomposed by the caustic alkalies with the evolution of hydrogen. It has a powerful reducing action.

Chryseon, or **Silicone** ($Si_6H_6O_4$?) is an orange-coloured body, insoluble in most solvents. It is decomposed by sunlight, and is a powerful reducing agent.

No compound of carbon and silicon is known.

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CHAPTER IX.

HYDROGEN.

HYDROGEN:—Compounds of Hydrogen and Oxygen—Water—Compounds of Hydrogen with the Haloids, with Nitrogen, with Phosphorus, with Sulphur and Selenium—Compounds with Carbon, viz., Methane, Ethylene and Acetylene—Flame—Compound of Hydrogen and Silicon.

HYDROGEN (H = 1).

Atomic weight, 1. *Molecular weight*, 2. *Molecular volume*, $\square\square$. *Relative weight*, 1. *Specific gravity*, 0·0693. 100 *cubic inches weigh* 2·1496 *grains, and* 1 *litre* = 1 *crith, i.e., weighs* 0·0896 *grm.* 1 *grm. at* 0° *C. and at* 760 *mm. pressure measures* 11·19 *litres, and* 1 *grain at* 60° *F. and* 30 *B.P. measures* 46·73 *cubic inches.*

Synonyms.—*Inflammable Air or Gas* (Cavendish, 1781); *Phlogiston* (older chemists); *Hydrogen* (ὑδωρ water, and γενναω I produce) (Associated French Chemists).

History.—The alchymists described "an inflammable air," which was, no doubt, hydrogen. It was studied by Paracelsus in the sixteenth, and by Hales in the seventeenth century, when engaged in examining the gas produced by the distillation of coal. Cavendish (1766) examined it more carefully, and was the first to set it free by the action of acids on metals. Its properties were afterwards investigated by Watt, Priestley, Volta, and others.

Natural History.—(α.) *In the mineral kingdom* it is found free in volcanic gases (to the extent, at times, of 25 per cent.), in firedamp, and also occluded in meteorites (*see* page 193). In a combined state, it forms one-ninth part by weight of water, three-seventeenths of ammonia, one seventeenth of sulphuretted hydrogen, etc. (β.) *In the vegetable kingdom* it is found as a constituent of all tissues, as well as in the water with which in all cases the tissue is associated; whilst (γ.) *In the animal kingdom* it is always found in the tissues, and occasionally in a free state in the breath.

Preparation.—(1.) By the electrolysis of water, the hydrogen being developed at the negative pole.

(2.) By the action of an intense heat on water.

(3.) By the action of sodium and potassium on water at common temperatures.

$$2H_2O + Na_2 = 2NaHO + H_2.$$

Water + Sodium = Sodic hydrate + Hydrogen.

$$(2OH_2 + Na_2 = 2ONaH + H_2.)$$

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(4.) By passing steam over certain red hot metals, such as iron.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$
Iron + Water = Triferric tetroxide (Black or magnetic oxide) + Hydrogen.

$$(Fe_3 + 4OH_2 = Fe_3O_4 + 4H_2.$$

[NOTE.—Metallic platinum cannot be made to decompose water at any temperature, but if the platinum be intimately associated with magnesium or with zinc, decomposition of the water may be effected at ordinary temperatures. Copper decomposes water at a very high temperature, but if the copper be associated with zinc it then decomposes it at ordinary temperatures. (Proceedings of R. S., 1872, pp. 133, 218.])

(5.) By passing steam over red hot coke or charcoal (Deville and Debray):—

$$2H_2O + C = 2H_2 + CO_2.$$
Water + Carbon = Hydrogen + Carbonic anhydride.

$$[2OH_2 + C = 2H_2 + CO_2].$$

[NOTE.—The CO_2 may be removed by lime. If the heat be too great, CO (and not CO_2) is formed, this gas being incapable of removal by lime].

(6.) By the action of hydrochloric or dilute sulphuric acid on zinc and on certain other metals:—

(α.)
$$Zn + 2HCl = ZnCl_2 + H_2.$$
Zinc + Hydrochloric acid. = Zincic Chloride + Hydrogen.
$$[Zn + 2HCl = ZnCl_2 + H_2.]$$

(β.)
$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$
Zinc + Sulphuric acid = Zincic sulphate + Hydrogen.
$$[Zn + SO_2Ho_2 = SO_2Zno'' + H_2.]$$

[NOTE.—(α.) On closing the vessel in which hydrogen is being generated by the action of dilute sulphuric acid on zinc, the pressure of the gas stops further decomposition. It has been suggested that, in this case, pressure stops affinity by preventing the escape of bubbles of hydrogen, the effect of which ordinarily is to displace the zincic sulphate solution immediately surrounding the zinc. This being stopped, fresh acid is prevented from coming into contact with the metal. (β.) The hydrogen prepared by the action of acids on metals is not pure, but contains certain compounds of H and C, which may be removed by passing the gas through wood charcoal, and also of H and S, and H and As. It may be purified from these latter by passing it through solutions of caustic potash and argentic nitrate respectively.]

(7.) By boiling zinc in a solution of potassic hydrate, the zinc displacing the hydrogen:—

$$2KHO + Zn = ZnK_2O_2 + H_2.$$
Potassic hydrate + Zinc = Potassic zincic oxide + Hydrogen.

$$[2OKH + Zn = ZnKo_2 + H_2.]$$

(8.) By submitting certain organic substances to destructive distillation.

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Properties.—(α.) *Sensible.*—When pure, hydrogen is a colorless gas, without taste or odor.

(β.) *Physiological.*—It has no toxic effects. It may be breathed for a few seconds (when pure) with impunity, the voice being rendered peculiarly shrill under its influence. If breathed continuously, death results from want of oxygen.

(γ.) *Physical.*—Hydrogen is the lightest body known, being 14·47 times lighter than air (Sp. Gr. 0·0693). Sound travels three times faster in it than in air. It is a permanent gas, that is, no cold or pressure can effect its condensation. It refracts light more powerfully than any other gas; compared with air, at the same temperature and density, its refracting power is six times as great. Hydrogen exhibits in a remarkable degree the power of *diffusion, i. e.*, a power due to the constant motion and mutual repulsion of gas particles. If a bottle of hydrogen be connected vertically, by a narrow glass tube, with a bottle of oxygen, the oxygen (the heavier gas) being below, the hydrogen, against the action of gravity, will descend, and the oxygen will ascend, a complete mixture of the gases in the two bottles resulting. Similarly, if a vessel be divided into two parts by a porous diaphragm, one-half being filled with one gas and the other half with another gas, diffusion will take place until the admixture of the gases is complete. But the rate of diffusion is not alike. Graham's law is expressed thus:—"*The diffusibility of two gases varies inversely as the square roots of their densities.*" Thus, the density of H = 1 and of O = 16, therefore the diffusibility of these two gases is as 4 to 1; in other words, the diffusion of four cubic inches of hydrogen will occupy the same time as the diffusion of one cubic inch of oxygen.

The "*diffusiometer*" of Graham is a glass tube closed at one end by some porous material, such as well-dried plaster of Paris. If this be filled with hydrogen and the open end placed in water, the water rises rapidly in the tube, because the hydrogen passes through the porous diaphragm (*i. e.* diffuses) at a greater rate than the air enters; *i. e.*, H = 1 and air = 14·47, therefore their relative diffusibility = $\sqrt{14{\cdot}47}$ to $\sqrt{1}$, or as 3·8 to 1; or, for every 1 cubic inch of air entering the tube, 3·8 cubic inches of hydrogen escape. It will be seen, therefore, that by this means a mixture of two gases of unequal diffusibility may be partially separated (*atmolysis*).

By the term *osmosis*, we imply not simply diffusion through small apertures, but the passage through membranous diaphragms. Here, adhesion between the membrane and the gas plays its part in the process, as well as diffusion.

We have remarked that hydrogen is found *occluded*, that is, absorbed, in meteoric iron. If hydrogen be passed over a red-hot plate of platinum, the metal will absorb 3·8 times its own volume of the gas, whilst palladium will absorb 376 volumes at common temperatures, 643 volumes at 194° F. (90° C.), and 526 volumes at 473° F.

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(245° C.), the occluded hydrogen being in every case completely evolved on the application of heat. The absorbed gas possesses great chemical activity, for if the palladium containing the occluded hydrogen be placed in a jar of chlorine, or in an iodine solution, hydrochloric and hydriodic acids will be formed; and, by similar means, ferric oxide may be changed to ferrous oxide. Graham held that in this and like cases an alloy of palladium or other metal and hydrogen (to which, in this state, he gave the name "*hydrogenium*") was formed, but of this there is considerable doubt.

The analogy between hydrogen and the metals is well marked, nor is the fact of its gaseous condition any argument against its metallic nature.

(δ.) *Chemical.*—Hydrogen has no action on litmus or turmeric. It will not support combustion, but it burns, when pure, with a perfectly colorless flame, any color being probably due to some impurity, such as a trace of sulphur either in the air or in the gas. Water is the only product of its combustion (noted by Macquer, 1766). In burning, it produces a greater heat than an equal bulk of any known substance; one grain of hydrogen, in combining with eight grains of oxygen, produces sufficient heat to raise 62,031 grains of water 1° F., or 34,462 grains 1° C.

With *oxygen*, hydrogen does not combine under ordinary circumstances; but by the action of heat, or by spongy platinum, or when the gases are nascent, combination may be easily effected. [The explosion resulting from firing the mixed gases depends on the sudden expansion caused by the heat developed by the combination.]

In the case of the *haloids*, heat is required to effect the chemical union of hydrogen with iodine and fluorine, whilst daylight is sufficient to effect its combination with chlorine and bromine.

With *nitrogen*, combination may be effected directly, if the gas be in a nascent state, when ammonia is formed.

With *carbon* and *sulphur*, the *direct* union, and with *phosphorus*, *selenium*, *silicon*, etc., the *indirect* union of hydrogen may be effected.

With *antimony* and *arsenic*, hydrogen, when nascent, forms gaseous combinations.

Water dissolves a trace of hydrogen; 100 volumes take up 1·93 volumes of the gas, its solubility being unaffected by the temperature of the solvent.

The *acids* have no action upon it, except that nascent hydrogen reduces nitric acid.

The *alkalies* are also without action upon it.

With the *metals*, hydrogen forms but few compounds.

Metallic oxides are unaffected by hydrogen, unless they be red hot, when they are reduced.

Comparing hydrogen with oxygen, we may note their remarkable chemical dissimilarity; oxygen combines with all the elements (and

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commonly directly) except with fluorine, whereas the hydrogen compound with fluorine is easily formed and of great stability; moreover, hydrogen combines directly with none of the elements except with oxygen, carbon, sulphur, and the haloids (fluorine excepted). The combining power between oxygen and the metals is intense, whilst that between hydrogen and the metals is almost *nil*.

Its proportion in gaseous mixtures may be determined by a eudiometric experiment, as already described (page 98).

COMPOUNDS OF HYDROGEN AND OXYGEN.

Water ... ... H_2O.
Peroxide of hydrogen ... ... H_2O_2.

WATER (H_2O or OH_2).

Molecular weight, 18; *Density*, 9; *Specific gravity*, 1·000.

History.—Water was regarded by the ancients as an element. Thales (600 B.C.) describes it as the origin of all things; Van Helmont (1600 A.D.) estimated the quantities present in various animal, vegetable, and mineral compounds. Priestley (1780) correctly predicted its composition from noting the moisture formed on firing a mixture of air and hydrogen. Watt and Cavendish (1781-1783) confirmed Priestley's predictions by more accurate experiments, proving its compound nature and the proportions of its constituents. Lavoisier and Laplace (1783-4) added further confirmatory proofs of its exact composition.

Natural History.—(*α.*) In the *mineral* kingdom it is found as water, in (*a*) the atmosphere, also as rain, snow, and hail; and (*b*) in seas and rivers. It is estimated that $\frac{3}{4}$ of the earth's surface, or 32,000,000 cubic miles is water. It also occurs (*c*) below the surface of the earth to a certain depth, thrown up here and there as springs, and (*d*) lastly, combined in many minerals as hydrates. (*β.*) In the *vegetable kingdom*, and (*γ.*) also in the *animal* kingdom, a large percentage is water.

Preparation.—Chemically pure water is not found in nature. It may be prepared by *distillation*, that is, by vaporizing the water and condensing the vapor. *Filtration* removes suspended matters only.

Composition.

		By volumes.	By weight (atomic).	By weight (percentage).
Hydrogen ...	H_2 =	2	2	11·11
Oxygen ...	O =	1	16	88·89
	H_2O=	3	18	100·00

The two volumes of hydrogen combining with one volume of oxygen form two volumes of water gas.

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Proofs of its composition.—These are both analytical and synthetical.

(A.) *Analytical.* (1.) By the electrolysis of water.

Placing the platinum terminals of a galvanic battery in a weak acid solution, the acid being added to increase the conductivity of the water, hydrogen will be immediately evolved from the negative, and oxygen from the positive pole. The volume of oxygen evolved is *slightly less* than one-half the volume of hydrogen. It should be exactly one-half, but (1) oxygen is more soluble than hydrogen in water, and (2) some of the oxygen is ozonized (as may be proved by its action on iodized starch paper), in which form three volumes are condensed into two. Allowing for this, the experiment proves that water is made up of 2 *volumes of hydrogen* + 1 *volume of oxygen.* The same fact might also be demonstrated by passing sparks from the induction coil through steam, whereby it is decomposed, and analyzing the products formed.

Oxygen is sixteen times heavier than hydrogen. The bulk of hydrogen in water being twice that of oxygen, it follows, therefore, that in 18 parts by weight of water we have 2 *parts by weight of hydrogen* + 16 *parts by weight of oxygen.*

(2.) That water is made up of oxygen and hydrogen in these proportions by weight may be proved by passing steam over a weighed quantity of red-hot iron, whereby the water is decomposed, hydrogen passing over in a free state, and an oxide of iron formed. The hydrogen may be measured and its weight estimated, whilst the weight of the oxygen in combination with the iron may also be determined.

(B.) *Synthetical.* (1.) If two volumes of hydrogen and one volume of oxygen be fired in a eudiometer by an electric spark, they combine with explosion, this being due to the energetic and rapid combination of the gases, attended with sudden expansion and great evolution of heat. The water gas (H_2O) formed will measure (when compared under identical conditions and at such a temperature that the water is in a state of gas) two-thirds the bulk of the original gas, or, in other words, three volumes of the mixed gases will be found to form two volumes of steam. (Cavendish.) (*See* page 34.)

It may further be noted that combination in these proportions is constant. If oxygen and hydrogen be mixed in arbitrary proportions and exploded, combination always occurs in the proportion of two volumes of hydrogen with one volume of oxygen, whilst the gas added in excess, remains unaltered after explosion.

(2.) If a stream of pure hydrogen be passed over a weighed quantity of hot and well-dried cupric oxide, the hydrogen will deprive the copper of its oxygen, and steam will be formed. If the water be collected and weighed, and the weight of the reduced copper be also estimated (loss=O), we shall be able to determine the relative weights of oxygen and hydrogen present in the water formed. (Dulong and Berzelius, Dumas and Boussingault).

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(3.) Water is the only product of the combustion of hydrogen in air or oxygen. And, moreover, whenever combustible bodies containing hydrogen, such as tallow, oil, coal gas, etc., burn with flame, water is always found as one product of the combustion.

It may here be noted that enormous heat is evolved by the union of hydrogen and oxygen. Thus, the oxy-hydrogen jet supplies us with a heat almost unsurpassed by chemical means.

Properties.—(α.) *Sensible.*—Water (when pure) is usually said to have neither color, taste, nor smell. As regards its *color*, we note that when a layer of six feet is examined by transmitted light, it appears of a blue tint, and in still greater bulk, as seen in the Swiss lakes, of a bluish green tint. The presence of organic matter, however, even in minute quantity, imparts a brownish tinge to the water, so much so, that the tint-depth may be taken as a rough indication of the amount of organic matter present in solution.

As regards its *odor*, although this cannot be detected by man, animals smell it at long distances, as shown in the case of horses and camels in the desert.

Physical.—(β.) The specific gravity of water at 39·2° F. (4° C.), (its point of maximum density) is regarded as 1·000, and is the standard of comparison for solids and liquids.

Water may exist in the *solid*, *liquid* or *gaseous* state. The change from the solid into the liquid, or from the liquid into the gaseous state, involves the absorption of heat.

As to its *weight*—

1 cub. in. of water weighs (62° F. or 16·7° C.) 252·456 grs., Sp. Gr. 1·000
,, of ice ,, (32° F. or 0° C.) 235·000 grs., Sp. Gr. 0·91674
,, of steam ,, (212° F. or 100° C.) 0·1932 gr., Sp. Gr. 0·623 (0·0693×9)

Water is therefore about 825 times heavier than air. A *cubic foot* weighs about 1000 ozs. avoird. (actually 997 ozs.); *one gallon*, 70,000 grains, or about 10 lbs. avoird.; 1 *litre* (at 4° C.), 1000 grammes, or 1 kilogramme.

Water is practically incompressible. Every atmosphere contracts it about fifty-one-millionths of its bulk, or a presssure of 30,000 lbs. will force 14 volumes into 13. (Regnault.)

The action of heat.—At all temperatures, water evaporates. At 32° F. (0° C.) it freezes. If this frozen water be heated it melts, but until the whole of the ice be melted the liquid remains at 32° F. (0° C.), notwithstanding the application of heat. After the ice is melted, its temperature gradually rises as the heat is continued up to 212° F. (100° C.), when the water boils, whilst if the heat be applied long enough, the water will entirely boil away.

I.—We say, then, water freezes or becomes solid at 32° F. or 0° C. But the exact temperature of freezing is influenced by a variety of circumstances. The *melting point of ice* is more constant than the *freezing point of water*; hence, the former is usually employed in

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graduating thermometers. The circumstances influencing the temperature of freezing are as follows:—

(α.) The presence of atmospheric air. In closed vessels, at perfect rest and *out of contact with air*, the temperature of water may be lowered to 14° F. (−10° C.) without solidification, but if the water at this temperature be shaken, it instantly freezes, the temperature immediately rising to 32° F. (0° C.).

(β.) In closed vessels, *air being present*, or in very narrow tubes, water may be cooled to 5° F. (−15° C.) without its becoming frozen, solidification occurring on the slightest motion being imparted to the liquid.

(γ.) If water be surrounded by certain mixtures (such as chloroform and sweet almond oil, which may be mixed in such proportions that the liquid has the same density as water), the water thus encircled may be cooled, without solidifying, to −4° F. (−20° C.). If, in this state, however, it be touched with a piece of ice, it instantly freezes and expands.

(δ.) Pressure.—The melting point is lowered 0·0075° C. for every additional atmosphere. At a pressure, therefore, of 13,000 atmospheres, ice would be converted into water at 0·4° F. (−18° C.) Water at 39·2° F. (4° C.), enclosed in a perfectly tight vessel where expansion is impossible, will not freeze although cooled below zero. The ice crystals are rhombohedric and six-sided prisms.

II. On heating ice at 32° F. (0° C.), we note that the application of heat does not raise the temperature until the whole of the ice is melted. Thus, *ice* at 32° F. (0° C.) *uses up* heat to become *water* at 32° F. (0° C.). The amount of heat thus used up by a given amount of *ice* is called *the latent heat of water*. A pound of *water* at 32° F. (0° C.) mixed with a pound of water at 175° F. (79·44° C.) will have a mean temperature of $\frac{32+175}{2}=103{\cdot}5°$ F., whilst a pound of *ice* at 32° F. (0° C.), mixed with a pound of water 175° F. (79·44° C.) will have a temperature of 32° F., *but the ice will have melted*, 143 degrees F. having been required for this purpose. Note, therefore,

$$175 - 143 = 32\text{; temperature of liquid} = \frac{32 + 32}{2} = 32° \text{ F.}$$

We regard, therefore, 143° F. (79·4° C.) *as the latent heat of water;* in other words, 143° F. (79·4° C.) is the heat, unrecognisable by a thermometer, absorbed by 1 lb. of ice in becoming water.

[For explanation of thermal unit, or unit of heat, *vide* page 37.]

III.—Ice presents a peculiar phenomenon termed "*Regelation.*" Two pieces of ice, on being squeezed together, cohere. This cohesion ("regelation") is probably due to a certain portion of the ice becoming melted at the points of contact, owing to the melting point being lowered by the pressure. Instantly, however, that the pressure is removed, the water solidifies.

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IV. After a sufficiency of heat has been applied, the water boils. Water evaporates (that is, gives off vapor) at all temperatures. The vapor thus given off has a certain "elastic power," or "*tension.*" Air also has an "elastic power," or "tension," which is capable of supporting 760 mm., or nearly 30 inches of mercury; in other words, air has an elastic power capable of exerting a pressure of 15lbs. on every square inch. When the tension or pressure of the vapor given off by the water under the action of heat, balances the tension or pressure of the atmosphere, the water is said to boil. This occurs at 212° F. (100° C.).

V. Various circumstances influence the temperature at which water boils.

(*a.*) Boiling, we have said, is the "temperature at which the pressure or the tension of the water-vapor balances the pressure of the atmosphere;" thus inasmuch as the pressure of the atmosphere constantly varies, it follows that the boiling-point of water must also vary. It is only when the barometer is at 760 mm. (that is, the mean height of the barometer at the sea-level) that water boils at 100° C., the boiling point being reduced 1° C. for every 27 mm. that the barometer falls. If water be placed under the exhausted receiver of an air-pump it may be made to boil even at common temperatures. On Mont Blanc (417 mm. pressure), water boils at 183·2° F. (84° C.). It will be seen, therefore, that by noting the temperature at which water boils, by means of what are called *hypsometric thermometers*, we may infer, approximately, the elevation. For every 590 feet the boiling point is lowered about 1° F. (1° C.) for every 1,062 feet.

The following table gives the tension of aqueous vapor at different temperatures. It will be noted that at 212° F. (100° C.), the vapor tension of water is equal to the pressure of the atmosphere (760 mm.). Hence water boils at 212° F. (100° C.):—

Tension of the vapor of water (Regnault.)

Temperature.		Tension in Mm. of Mercury.	Temperature.		Tension in Mm. of Mercury.
°F.	°C.		°F.	°C.	
— 4	—20	0·927	104	40	54·906
+14	—10	2·093	122	50	91·982
32	0	4·600	140	60	148·791
41	+ 5	6·534	158	70	233·093
50	10	9·165	176	80	354·280
59	15	12·699	194	90	525·450
68	20	17·391	212	100	760·000
86	30	31·548			

The above diagram will show the importance when graduating thermometers, of accurately noting the barometric pressure at the time of graduation.

Further, by *increasing* the atmospheric pressure the temperature at

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which water boils will also be increased. With one atmosphere (*i.e.*, 760 mm. pressure) we have seen that water boils at 212° F. (100° C.); with two atmospheres it requires a heat of 249° F. (120·6° C.); with three atmospheres, of 273° F. (133·9° C.); with ten atmospheres, of 356·5° F. (180·3° C.); with twenty atmospheres, of 415·4° F. (213° C.); and so on.

(β.) The boiling point varies with the purity of the liquid:—

A saturated solution of	sodic carbonate	boils at	104·6° C. or 220·2° F.
,, ,,	,, sodic chloride	,,	108·4° C. or 227·0° F.
,, ,,	,, potassic nitrate	,,	115·9° C. or 240·6° F.
,, ,,	,, sodic nitrate	,,	121·0° C. or 249·8° F.
,, ,,	,, potassic carbonate	,,	133·0° C. or 271·4° F.
,, ,,	,, calcic chloride	,,	179·5° C. or 355·1° F.

(γ.) The boiling point depends on the depth of the bulk heated. A column 32 feet deep would not *completely* boil—that is, give off vapor from the bottom of the vessel—at a lower temperature than 249·8° F. (121° C.)

(δ.) The boiling point varies with the vessel in which the water is boiled. The adhesion of water for glass is greater than the adhesion of water for metal. This adhesion must be overcome; and hence, in the case of very clean glass, the adhesion between the glass and the water particles may raise the boiling point 1 or 2 degrees.

(ε.) In boiling, the cohesion of the particles of water for one another has also to be overcome by heat. The presence of gases in solution lowers the boiling point by destroying this attraction of the water particles, and, conversely, the absence of dissolved gases heightens the boiling point.

VI. *The latent heat of steam* is said to be 997° F., or 537° C. (*i.e.*, 537 thermal units), that is, the heat required to boil away 1 lb. of water at 212° F. (160° C.), will raise 5·37lbs. of water from 32° to 212° F. (=180 degrees F.), [or from 0° to 100° C. (=100 degrees C.)]; or if the steam from 1 lb. of water be conveyed into 5·37 lbs. of water at 32° F. (0° C.), it will raise it to 212° F. (100° C.).

$$(180 \times 5{\cdot}37 = 996{\cdot}66, \text{ or } 100 \times 5{\cdot}37 = 537).$$

VII. If a drop of water be placed on a red-hot platinum dish, it assumes what is called *the spheroidal condition*; that is, the spheroid rests on a cushion of its own vapor, which, being a bad conductor of heat, prevents the spheroid of water boiling. The temperature of the spheroid has been ascertained to be about 194° F. (90° C.), and the space between the spheroid and the dish to be about 0·15 to 0·25 mm.

VIII. On subjecting water to the action of intense cold, it gradually contracts to 39·2° F. (4° C.). This temperature is what is called "*the maximum density of water.*" [We should note that the presence of soluble salts lowers the maximum density, so that in sea-water it is below 32° F. (0° C.)] At this point of maximum density

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a given bulk of water weighs more than at any other temperature. Hence 1 c.c. of water, at 39·2° F., or 4° C., is taken as representing a gramme weight. Below 39·2° F. (4° C.) water expands rapidly, so that ice floats on water, owing to its less specific gravity. (1 volume of water at 0° C. becomes 1·09082 volume of ice). Thus water-pipes break, rocks disintegrate, and rivers and lakes freeze only on the surface, the ice easily melting as the warm weather returns. At 39·2° F. (4° C.) convection in (*i.e.*, the circulation of) rivers and lakes ceases.

When water is heated from 39·2° F. (4° C.) it expands; 1 volume of water at 39·2° F. (4° C.), becoming 1·04312 volumes at 212° F. (100° C.).

We may here note that aqueous vapour is very opaque to heat. Thus the moisture of the air prevents radiation from the earth.

Water is a simple refractor of light, its refracting power increasing as it is cooled, this increase of refraction not being interfered with by its expansion below 39·2° F. (4° C). (Arago and Fresnel.)

Water as a neutral solvent is unsurpassed. Solution is generally a purely *physical* act, neither heat nor change of property resulting. The act of liquefaction (*i.e.*, the passage from a solid to a liquid) is usually accompanied by cold (*i.e.*, the absorption of heat).

I. *Solubility of solids in water.*—The *rapidity* with which a solid dissolves depends—(1) on whether the solid be in lump, or finely powdered; and (2), on the motion imparted to the mixture. In the *first* case, powdering the body increases the surface upon which the water acts; and in the *second*, motion removes the saturated solution surrounding the solid, thus bringing fresh and unsaturated portions of the solvent into contact with the material. If such motion be not imparted to the menstruum during the period of action, solution is slow and only proceeds by "*liquid diffusion*" (a process analogous to "*gaseous diffusion*"), *i. e., the passage of a solution of one salt into a solution of a second salt* contrary to gravity. This diffusive power varies with different bodies. It is rapid with potassic chloride, and with most crystalline bodies, but slow with gelatine and with most jelly-like bodies. Bodies that diffuse rapidly are called "*crystalloids*," and bodies that diffuse slowly or not at all, "*colloids*." This diffusion of certain bodies and non-diffusion of others takes place equally well if a membrane separates the two liquids (Dialysis), the rapidity with which one liquid passes through the membrane into the second, in no way necessarily representing the rate at which the second passes through and into the first.

In describing the solubility of solids, it is usual to state the number of parts of *anhydrous* salt taken up by 100 parts of water at a given temperature.

Ordinarily the solubility of a body increases, as the temperature increases. If a boiling solution of a salt be allowed to cool, *exposed*

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to the air, a certain portion of the salt crystallizes out and the clear solution, at normal temperatures, is termed "*a saturated solution*," *i. e.*, a solution which at that temperature can dissolve no more of the salt; but if it be allowed to cool *out of contact with air*, a larger quantity of the salt is then held in solution, and this is termed "*a supersaturated solution*," from which, however, the excess of solid matter may often be separated by slight physical disturbances, such as motion, dust, or dropping into the solution a minute fragment of the salt.

A saturated solution of one salt will often dissolve an appreciable amount of a second salt.

The influence of temperature on solubility is not constant.

(1.) The solubility, for instance, of *potassic chloride* is directly as the temperature, but the solubility of *potassic chlorate* increases far more rapidly than the temperature.

(2.) The solubility of some bodies, such as *sodic chloride*, is the same at all temperatures.

(3.) The solubility, in some cases, decreases as the water is heated. Thus *lime*, is twice as soluble in water at 32° F. (0° C.) as it is in water at 212° F. (100° C.). One part of strontic sulphate requires 7,000 parts of water at 57·2° F. (14° C.) and 9600 parts at 212° F. (100° C.) for complete solution.

(4.) Occasionally the maximum solubility of substances is at a temperature a little above the common temperature, and decreases if the temperature be raised. Thus at 32° F. (0° C.) 1 part of *calcic sulphate* is soluble in 488 parts of water, but at 95° F. (35° C.) 1 part is soluble in 393 of water. This is the point of maximum solubility of calcic sulphate in water, and from this point its solubility decreases, for, at 212° F. (100° C.) 1 part requires 460 of water for solution.

Water, when "*super-heated*," *i. e.*, heated under pressure, possesses greatly increased solvent powers. Thus, at 300° F. (149° C.) water dissolves glass. Possibly the solution of silica in the Geyser springs, may be accounted for by the action of water, superheated by internal pressure.

II. *Solubility of liquids in water.*—By this is implied the miscibility or the blending of liquids. Water mixes with alcohol. If the water be in excess the water is regarded as the solvent, but the alcohol if it be in excess.

III. *Solubility of gases.* — All gases are more or less soluble in water—*i.e.*, are more or less *absorbed* by water—but all gases are not equally soluble.

The '*coefficient of solubility*,' or '*absorption coefficient*,' as it is called, is the volume of gas absorbed by one volume of water at 59° F. (15° C.)

The following table exhibits the absorption or solution of various gases.

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Gas at 59° F. (B.P. 30).	Vol. dissolved by one vol. of water at 59° F. (15° C.) and 30 B.P.	Vol. dissolved by one vol. of water at 32° F. (0° C.) and 30 B.P.
Hydrogen	·0193	·0193
Nitrogen	·0148	·0203
Carbonic oxide	·0243	·0328
Oxygen	·0299	·0411
Marsh gas	·0391	·0545
Olefiant gas	·1615	·2563
Nitrous oxide	·7780	1·3052
Carbonic acid	1·0000	1·7967
Chlorine	2·5680	—
Sulphuretted hydrogen	3·2326	4·3706
Sulphurous acid	43·5640	68·8610
Hydrochloric acid	457·8000	505·8000
Ammonia..	782·7000	1148·0000

[NOTE.—The absorption coefficient is often stated as the volume of gas at 0° C. and 766 mm. absorbed by 1 c.c. of liquid at 0° C. and 766 mm.]

The solubility of a gas in water (and, indeed, in all other solvents) is influenced by certain circumstances.

(1.) *The temperature of the solvent.*—The general law may be thus stated:—*The volume of gas dissolved increases as the temperature of the solvent decreases.* But note—

(α.) In the case of hydrogen, the solubility remains the same for all temperatures.

(β.) The law is only true so long as the solvent remains liquid, for directly the liquid freezes, the dissolved gases are *usually* liberated. But exceptions to this rule are found in the case of condensible gases, such as carbonic anhydride, and in the case of those gases such as chlorine, which form definite chemical compounds with water.

When the solvent is boiled, the dissolved gas is, as a rule, entirely evolved. In the case, however, of those gases that are very soluble (such as hydrochloric acid gas), mere boiling never effects the entire expulsion of the gas. The solution having become of a certain strength, remains constant, evaporation to dryness being the only means of effecting the complete removal of the remainder.

(2.) *The degree of pressure.*—In the case of the moderately soluble, but not in the case of the very soluble gases, Dalton and Henry's law holds good, that "*the volume of gas absorbed, varies directly with the pressure.*" With a pressure, *e.g.*, of one atmosphere, one volume of water at 0° C. dissolves 1·18 volumes of CO_2; with $\frac{1}{2}$ atmosphere, $\left(\frac{1{\cdot}18}{2} = \right)$ 0·59 volume; with 2 atmospheres, (1·18 × 2=) 2·36 volumes, etc.

By placing a solution of gas in a vacuum, its almost entire removal from the solvent may be effected. It may be noted, moreover, that a similar withdrawal may often be effected by exposing the solution of one gas to an atmosphere of a second gas.

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We have now to consider *the action of solvents on a mixture of gases.*—Good drinking water should be well aerated, *i.e.*, should contain a certain quantity of dissolved gas. Every gallon of water should yield 7 to 8 cubic inches of gas, or about 4 cubic inches of nitrogen, 2 cubic inches of oxygen, and 1 cubic inch of carbonic anhydride. These gases are dissolved by the water from the air. But air is a mixture of 1 part of oxygen to 4 parts of nitrogen (exactly as 21 to 79), whereas the dissolved gas is in the proportion of 1 of oxygen to 2 of nitrogen. How is it, then, that the ratio of the gases dissolved by the water, is not the same as that in which they are present in the air?

In a mixed gas the solution of the several constituents does not depend on the *general* pressure, but on *the pressure exerted by each gas* 'per se.' For example, to take a simple case: If we act with water on a mixture of one volume of oxygen and three volumes of nitrogen under a pressure of four atmospheres, we shall find that the oxygen dissolved, will be that quantity that the water can absorb under one atmosphere (*i.e.*, the $\frac{1}{4}$th of four atmospheres); and the nitrogen, the quantity the water can absorb under a pressure of three atmospheres (*i.e.*, $\frac{3}{4}$ths of four atmospheres). So with air, $\frac{1}{5}$th of which is oxygen and $\frac{4}{5}$ths nitrogen, the pressure of the whole being one atmosphere. The quantity of each gas dissolved will be found by multiplying the proportion of the gas in the mixture, by its co-efficient of solubility; thus—

0·0299 (coefficient of absorption of oxygen) $\times \frac{1}{5}$ (proportion of oxygen in air)=0·00598
0·0148 (do. do. of nitrogen) $\times \frac{4}{5}$ (do. of nitrogen do.) =0·01184

0·01782

Therefore, of every 0·01782 volumes of air dissolved by water, 0·00598 will be oxygen and 0·01184 nitrogen; that is, in about the proportion of two of nitrogen to one of oxygen. Thus, the air dissolved by water is richer in oxygen than the atmosphere. This oxygen is present in the water, not only for the support of water-animal life, but for its own self-purification, whereby harmful products are changed into harmless products by oxidation. The carbonic acid, too, plays its part in rock disintegration and in soil-formation.

Water dissolves *the haloid* elements, and is slowly decomposed by them with the evolution of oxygen ($H_2O + Cl_2 = 2HCl + O$). On *the combustible solids* (carbon, etc.) it has little or no action unless it be heated, when it is decomposed ($C + H_2O = CO + H_2$). On *oxygen, nitrogen,* and *hydrogen,* its action is simply solution. The *metals* are attacked differently by it. (α.) Some, as *the alkaline metals* decompose it at ordinary temperatures; (β) others, as *magnesium,* decompose it if the water be boiling; (γ) others, as *iron, zinc,* etc.,

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decompose it when the metals are red hot; whilst (δ) *gold* and *platinum* require to be raised to a white heat in order to effect its decomposition.

(γ.) *Chemical.*—Water is without action either on litmus or turmeric. Chemically, it is an indifferent oxide. It unites with bodies in several ways to form hydrates. Thus—

(1.) *It unites with the anhydrides to form acids,* heat being evolved at the time of combination ($SO_3 + H_2O = H_2SO_4$). This water molecule cannot be afterwards separated from the anhydride, merely by the action of heat. Sulphuric acid, moreover, has a great affinity for water, and hence one of its common laboratory uses.

(2.) *It unites with bases to form hydrates,* heat being evolved at the time of combination. In some cases the water molecule cannot be driven off by heat (*e. g.*, KHO), whilst in other cases a red heat will effect its expulsion (*e. g.*, $CaH_2O_2 = CaO + H_2O$).

(3.) *It unites with certain bodies as water of crystallization, i.e.,* water connected with the shape and color of the crystal. This water of crystallization may be expelled at a temperature of 212° F. (100° C.), certain changes resulting. Thus, if blue *sulphate of copper* ($CuSO_4, 5H_2O$) be heated to 212° F. (100° C.), it loses four of its water molecules, becoming $CuSO_4, H_2O$, whilst at the same time it loses both shape and color. So again the pink hydrated chloride of cobalt ($CoCl_2 + 6aq$) forms when heated the blue anhydrous chloride ($CoCl_2$), which again becomes hydrous and pink on exposure to air (sympathetic ink). Similar changes of color are well marked in the magnesic-platino-cyanide, which is green, red, yellow, or white, according to the quantity of water of crystallization it contains. Some salts (as *e. g.*, NaCl) contain no water of crystallization, whilst in many others (as *e. g.*, sodic sulphate, borax, etc.), the number of water molecules may be made to vary, different crystalline shapes resulting.

In some cases (as *e.g.*, sodic carbonate), bodies part with their water of crystallization at ordinary temperatures (*effloresce*); whilst in many others (as *e.g.*, potassic carbonate) they take in more water on exposure, and melt (*deliquesce*). Thus calcic chloride is used in the laboratory as a desiccating agent.

(4.) *It unites in certain cases as water of constitution, or water of halhydration, i.e.,* as water associated with the chemical properties of bodies. Thus, a crystal of magnesic sulphate contains 7 molecules of water ($MgSO_4, 7H_2O$). If this be heated to 212° F. (100° C.), 6 molecules (water of crystallization) are driven off, and the salt is represented by the formula $MgSO_4, H_2O$. No heat, however, short of 410° F. (210° C.) will effect the removal of this last water molecule, and when the salt is heated to this temperature, it begins to decompose. It is clear, therefore, that this last water molecule is bound to the salt by a closer attraction than the other six molecules, and is termed "*water of constitution.*"

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This constitutional molecule of water may often be replaced by another salt, whereby a double salt is formed. Thus, $MgSO_4,H_2O + 6H_2O$ may be made to form $MgSO_4,K_2SO_4 + 6H_2O$, where K_2SO_4 replaces the molecule of constitutional water.

In order to express these two forms of water in a salt, the water of constitution is often written in chemical symbol, and the water of crystallization as *aq* (*aqua*), thus, $MgSO_4H_2O + 6aq$.

(5.) Water may possibly exist in many organic bodies, such as sugar, starch, gum, etc., in a molecular form.

Varieties of Water.

I. Common Water.—(*a.*) *Rain Water.*—This is the purest form of water; but even in the country, and much more in towns in the neighbourhood of factories, it is always more or less contaminated with the various impurities present in the air. The rain always contains more or less sodic chloride, organic matter, ammonia, nitric acid, etc. If rain water has been allowed to come into contact with lead, it is certain to dissolve a small quantity of the metal.

The rain collected after a long continuance of wet, is the nearest approach we know of to pure natural water.

(*b.*) *Spring and Well Water.*—The total solids present in these may vary from 5 to 200 grains per gallon, their quantity and character being largely dependent on the chemical nature of the soil through which the water percolates. Calcic and magnesic carbonates and sulphates, with sodic chloride, are the salts most commonly present.

The presence of *nitrites* or an excess of *nitrates and chlorides*, frequently found in the shallow well waters of towns, usually indicate sewage pollution, the two first being the oxidized products of animal nitrogenized substances (ammonia and albuminoid bodies), and the last being derived from the common salt used as food.

Sodic carbonate is commonly found in those well waters (as in the deep wells of London) that have percolated through a bed of chalk. The organic matter in the water of wells and springs is usually very small. Carbonic acid is the chief and very often the only gas present in such waters. Its origin is, probably, either the subterranean decomposition of carbonates, or the oxidation of the carbon of organic matter. It serves to hold the earthy carbonates in solution. A spring-water will often exhibit a slight turbidity after standing, due to the carbonic acid escaping by the exposure of the water to air, and the consequent precipitation of a part, and often as much as one-third, of the total calcic or magnesic carbonate.

The temperature of spring-water varies from ice-cold to 167° F. (75° C.), as in the case of some of the Carlsbad springs. The deep springs are usually the hottest.

(*c.*) *Lake and Marsh Water* usually contain more or less organic

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matter. Lake water is of excessively variable composition, being sometimes very pure (as *e. g.*, Loch Katrine), but at other times loaded with saline matter.

(*d.*) *River Water.*—Its composition depends much on the nature of the soil through which the river passes, and also on the extent of motion, the nature of the bed of the river, and the exposure the water undergoes. River water may be regarded as a mixture of rain, spring, and lake water. It differs from spring water generally, by being less clear (spring water undergoing natural filtration), and less sparkling (the carbonic acid present being in smaller quantity), and usually containing less solid matter. The organic matter present is derived from surface drainage and sewage; but this, after a sufficient run, if well diluted, is in a great measure got rid of, owing to the self-purifying action of the river.

II. Mineral Waters, *i. e.*, a spring water containing some medicinal ingredient. The names given to mineral waters depend on the predominating ingredient present; thus—

(*a.*) *Acidulous Waters,* from carbonic acid, which may be present in quantities varying from 30 to 200 cubic inches per gallon (Seltzer, Ilkeston, Spa, Pyrmont, etc.).

(*b.*) *Aperient Saline Waters,* from the presence of sulphates:—

(1.) Magnesic sulphate (Epsom, Leamington, etc.).

(2.) Sodic sulphate (Cheltenham, Scarborough, etc.).

(*c.*) *Calcareous Waters,* from calcic sulphate, or from calcic carbonate held in solution by carbonic acid (Matlock, Bath, Bristol, etc.).

(*d.*) *Chalybeate Waters,* from the presence of carbonate of iron held in solution by free carbonic acid (Pyrmont, Tunbridge, etc.). On exposure to air, Fe_2O_3, H_2O is precipitated ($2FeCO_3 + O + H_2O = Fe_2O_3, H_2O + 2CO_2$.)

(*e.*) *Brine,* from the presence of sodic chloride, bromide, and iodide (Middlewich, Shirleywich, Droitwich, etc.).

(*f.*) *Alkaline Waters,* from the presence of sodic carbonate and bicarbonate (Ems, Vichy, Malvern, etc.).

(*g.*) *Siliceous Waters,* from the presence of silica (Geysers).

(*h.*) *Sulphuretted* or *Hepatic Waters* (Harrogate, Aix-la-Chapelle, etc.).

(*i.*) *Sulphurous Waters* (Springs in the neighbourhood of volcanoes).

(*j.*) *Boracic Waters* (Lagoons of Tuscany).

III. Sea-Water.—Sea-water contains a large quantity of sodic and magnesic chlorides, to which its bitter saline taste is due, and to the hygroscopic character of which salts, the non-drying of clothes wetted with sea-water is to be attributed.

The following two analyses of sea-water may be quoted:—

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	British Channel (Schweizer).	Mediterranean (Usiglio).
Specific Gravity	1027·4 (at 16° C.)	1025·8 (at 21° C.)
Water	963·74372	962·345
Sodic chloride	28·05948	29·424
Potassic chloride	0·76552	0·505
Magnesic chloride	3·66658	3·219
,, bromide	0·02929	0·556
,, sulphate	2·29578	2·477
Calcic sulphate	1·40662	1·357
,, carbonate	0·03301	0·114
Iodine	traces.	
Ammonia	traces.	
Ferric oxide	..	0·003
	1000·00000	1000·000

The sea is the receptacle for the solid matters discharged by rivers, and dissolved by them from the earth. Their abstraction again from the sea and their return to the soil is effected by fish and marine plants.

IV. Water for Drinking Purposes.—It is important to determine—

(1.) Its *hardness*.—The terms "hard" and "soft," refer to the soap-destroying power of a water. Soap is an *alkaline stearate*. The addition to it of lime and magnesia decompose it, forming a *calcic* or *magnesic stearate*. Hence the reason why it is difficult to obtain "a lather" with hard water, (*i.e.*, a water containing lime and magnesian salts), viz., because a certain quantity of the soap is required to decompose the calcic and magnesian salts before a lather can be obtained, whilst, conversely, a lather is at once formed with a soft water, because of the absence of calcic and magnesic salts. Two kinds of hardness are usually described—(α.) *Temporary hardness, i.e., hardness due to calcic or magnesic carbonates*. These salts are almost insoluble in pure water, but are freely soluble in water containing carbonic acid (possibly as bicarbonates). On boiling, the carbonic acid is expelled and the carbonates are precipitated. Hence *temporary hardness* is that hardness which may be got rid of by boiling the water. (β.) *Permanent hardness, i.e., hardness due to calcic and magnesic sulphates*, etc. This is not got rid of by boiling. By the terms "*total*" or "*initial hardness*" we imply both the temporary and permanent hardness of a water.

In expressing the hardness of a water in degrees, it is to be understood that every degree, theoretically, represents 1 grain of calcic carbonate or its equivalent in soap-destroying power, in 1 gallon of water.

(2.) *Its action on lead.*—A water that acts freely on lead is not fitted for a town supply.

(3.) *Presence of organic matter*, which if of animal origin renders water unwholsome.

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Hydric Peroxide $(H_2O_2)\left\{\begin{matrix}OH\\OH.\end{matrix}\right.$

Molecular weight (probable), 36.

Synonyms.—*Peroxide of Hydrogen; Hydric Dioxide; Hydroxyl; Oxygenated Water.*

History.—Discovered by Thénard in 1818, and examined by Brodie and by Schönbein in 1850.

Preparation.—(1.) Peroxide of barium (prepared by heating caustic baryta (BaO) in a current of oxygen) is first mixed into a paste with water ($BaO_2,6H_2O$ being formed), and then added to dilute hydrochloric acid, surrounded by a freezing mixture.

$$\begin{matrix}BaO_26H_2O & + & 2HCl & = & H_2O_2 & + 6H_2O + & BaCl_2\\ \text{Hydrated baric peroxide} & + & \text{Hydrochloric acid} & = & \text{Hydric peroxide} & + \text{Water} + & \text{Baric chloride.}\end{matrix}$$

$$\left[\left\{\begin{matrix}O\\O\end{matrix}\right.Ba'',6OH_2 \quad + \quad 2HCl \quad = \quad \left\{\begin{matrix}OH\\OH\end{matrix}\right. \quad +6OH_2+ \quad BaCl_2.\right]$$

By decomposing the $BaCl_2$ with dilute sulphuric acid, HCl will be set free. The process then may be repeated until the liquid is of the required strength. Finally, the hydrochloric acid may be removed by argentic sulphate, and the sulphuric acid by baryta water.

(2.) By passing carbonic anhydride through a mixture of water and baric peroxide—

$$\begin{matrix}BaO_2 & + & CO_2 & + H_2O = & BaCO_3 & + & H_2O_2.\\ \text{Baric peroxide} & + & \text{Carbonic anhydride} & + \text{Water} = & \text{Baric carbonate} & + & \text{Hydric peroxide.}\end{matrix}$$

$$\left[\left\{\begin{matrix}O\\O\end{matrix}\right.Ba'' \quad + \quad CO_2 \quad + OH_2 = \quad COBao'' \quad + \quad \left\{\begin{matrix}OH.\\OH.\end{matrix}\right.\right]$$

(Similarly, it may be prepared by adding BaO_2 to dilute hydrofluoric acid, a baric fluoride being precipitated; or by adding potassic peroxide to a tartaric acid solution, a potassic tartrate being precipitated.)

Properties.—(α.) *Sensible and physiological.* A colorless and when concentrated a syrupy liquid, having a slight chlorous odor. It whitens the skin. It has a powerfully metallic, astringent taste, whitening and deadening the sensibility of the tongue, and rendering the saliva thick and viscid.

(β.) *Physical.* Specific gravity, 1·453. A temperature of 70° F. (21·1° C.) effects its slow decomposition, which becomes violent at 212° F. (100° C.), when the liquid evolves 475 times its volume of oxygen. It does not freeze at —22° F. (—30° C.). It mixes with water in all proportions.

(γ.) *Chemical.* Its reaction is neutral, but it bleaches litmus.

In contact with ozone, water is produced, and common oxygen set free. There is very little doubt but that the body described (page 63), as antozone is simply hydric peroxide, its antagonistic action to ozone being at once apparent by the following equation, ($H_2O_2 + O_3 = H_2O + 2O_2$). It forms water when acted on with nascent hydrogen ($H_2O_2 + Zn + H_2SO_4 = ZnSO_4 + 2H_2O$). It slowly

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decomposes, evolving oxygen, leaving common water. (This action is retarded by the presence of acids, and hastened by alkalies.) Its decomposition may be effected by powdered metals, such as gold, silver, platinum, etc., the metals themselves undergoing no change during the process (*see* Catalysis). As a chemical agent it has both oxidizing and reducing properties:—

(1.) *Oxidizing.* It bleaches litmus and indigo. It rapidly changes selenium, arsenicum, etc., into their highest oxides. It converts arsenious and sulphurous acids into arsenic and sulphuric acids; sulphide into sulphate of lead; the protoxides of iron, cobalt, calcium, etc., into peroxides, etc., etc.

(2.) *Reducing.* Mixed with the protoxides of silver, mercury, gold, etc., it not only loses its own oxygen but effects the reduction of the oxide ($Ag_2O + 2H_2O_2 = Ag_2 + H_2O + O_2$). Similarly it reduces the peroxides of manganese, lead, etc. ($MnO_2 + H_2O_2 = MnO + H_2O + O_2$). and also chromic and permanganic acids ($2CrO_3 + 3H_2O_2 = Cr_2O_3 + 3H_2O + 3O_2$), it being at the same time itself reduced.

It is to be noted that in all these cases the action is retarded by the presence of an acid, and aided by the presence of a free alkali.

Tests.—(1.) It liberates iodine from potassic iodide. ($H_2O_2 + 2KI = 2KHO + I_2$.)

(2.) When added to a solution of guiacum mixed with blood corpuscles, it turns it of a blue color. (Schönbein.)

(3.) If chromic anhydride (CrO_3) be added to a solution of hydric peroxide, an unstable perchromic oxide is first formed, Cr_2O_3 being the ultimate product. This compound is of a blue color and is soluble in ether, by which means its removal from the solution may be effected. This constitutes a very delicate test for hydroxyl.

Uses.—It has been used in medicine externally as a lotion and internally for diabetes and oxaluria. It constitutes the golden hair dye of the shops, the dyeing action being in reality a bleaching (oxidizing) action.

Compounds of Hydrogen and the Haloid Elements.

Hydrochloric Acid (HCl) (*Anhydrous*).

Molecular weight, 36·5. *Molecular volume*, $\boxed{\ |\ |\ }$. *Relative weight*, 18·25. *Specific gravity*, 1·27.

Synonyms.—*Spirit of Salts; Marine acid; Muriatic acid; Chloride of Hydrogen: Chlorhydric acid.*

History.—Probably known to Geber in the eighth century. The process of obtaining it from sulphuric acid and salt was first described by Glauber. Priestley (1772) was the first who obtained it as a gas. Its real nature was suspected by Scheele (1774), but it was believed by Berthollet and others to be an element, until Davy established the truth of Scheele's suspicions.

Natural History.—It is not found either in the animal or in

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the vegetable kingdom. It is found in the gases issuing from volcanoes and in the springs and rivers in their vicinity. It is found in the air over the sea, and in the neighbourhood of alkali works, etc.

Preparation.—(1.) By the direct combination of equal volumes of hydrogen and chlorine by heat, light or electricity. (Combination of these gases does not take place in the dark; in diffuse daylight combination is slow, whilst in sunlight the action is often accompanied by explosion.)

(2.) By burning hydrogen in chlorine.

(3.) By the action of dilute sulphuric acid on chlorides.

(*a.*) Prepared by this method in the laboratory in glass retorts *at a low temperature*, the reaction is as follows:—

$$H_2SO_4 + NaCl = NaHSO_4 + HCl.$$

Sulphuric acid + Sodic chloride = Hydric sodic sulphate + Hydrochloric acid.

$$[SO_2Ho_2 + NaCl = SO_2HoNao + HCl.]$$

(*β.*) Prepared commercially in iron retorts *at a high temperature*, the following reaction occurs:—

$$H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl.$$

Sulphuric acid + Sodic chloride = Sodic sulphate + Hydrochloric acid.

$$[SO_2Ho_2 + 2NaCl = SO_2Nao_2 + 2HCl.$$

(4.) By passing steam and chlorine through a red hot porcelain tube ($2H_2O + 2Cl_2 = 4HCl + O_2$.)

Properties.—(*a.*) *Sensible and physiological.*—A colorless, pungent smelling gas, having a strong acid taste. It is poisonous to animal life, and very destructive to vegetation, even when diluted with 25,000 parts of air.

(*b.*) *Physical.*—Specific gravity 1·27; 100 cub. in. (at 60° F. and 30 Bar. Pr.) weigh 39·23 grains, and 1 litre (0° C. and 760 mm.) 1·6352 grm. At a pressure of forty atmospheres at 50° F. (10° C.) it forms a colorless liquid, having a specific gravity of 1·27, less refracting than water, a solvent of bitumen, and with a very feeble action on litmus.

It has never been frozen.

The gas may be decomposed by electricity.

(*c.*) *Chemical.* Hydrochloric acid gas reddens litmus. It neither supports the combustion of a taper nor is itself combustible. Sodium and potassium burn in it. It acts on the metals, evolving hydrogen. It fumes in the air owing to its affinity for water, which absorbs from 480 to 500 times its bulk. The liquefied hydrochloric acid (anhydrous) dissolves solid litmus without reddening it, and, unlike the solution of the gas, is without action on iron, zinc, lime, etc., or even on the carbonates.

Hydrochloric Acid (*Solution*).

Preparation.—By dissolving the gas in water.

Properties.—(*a*) *Physical.* The liquid is colorless if pure, but more often it is slightly yellow. It fumes in the air. A solution

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containing *more* than 20 per cent. of the acid, evolves when heated hydrochloric acid gas; but if it contains *less* than 20 per cent. it then merely gives off water. A 20 per cent. acid distils unchanged. By electrolysis it may be split up into its constituent gases.

Its specific gravity varies with its strength. (See Table III. in Appendix.)

(β.) *Chemical.* A weak solution of the acid turns blue litmus red. Its action on the metals varies; some metals are freely dissolved by the cold acid with the evolution of hydrogen (K, Na, Ba, Fe, Zn, etc.); —others are only acted on by the boiling acid (Sn, Cu);—others are only slightly acted upon (Sb, Pb, Ag, Bi, etc.), whilst some are perfectly unaffected, either by the cold or by the boiling acid (Au, Pt, etc.). If, however, free chlorine be present in the acid solution, both gold and platinum are rapidly dissolved by it. On the *metallic oxides* it commonly forms water and a chloride of the metal corresponding to the oxide acted upon ($Fe_2O_3+6HCl=Fe_2Cl_6+3H_2O$), or if such compound does not exist, to one containing less chlorine than its equivalent oxygen ($PbO_2+4HCl=PbCl_2+2H_2O+Cl_2$).

Impurities.

(1.) *Sulphurous acid*, derived from the deoxidation of the sulphuric acid either by the organic matter of the salt, or by the metal of the still.

Test.—The evolution of sulphuretted hydrogen when zinc is added to the pure acid.

(2.) *Sulphuric acid*, which may be known by a soluble baryta salt producing a white precipitate of $BaSO_4$.

(3.) *Free chlorine*, which imparts a greenish yellow tint to the acid solution, may be known by its odor, and by the solution dissolving a little piece of gold leaf.

(4.) *Iodine and bromine* are sometimes present, derived from impurities in the common salt.

(5.) *Arsenious chloride*, derived from the sulphuric acid, may be known by the acid giving a yellow precipitate with sulphuretted hydrogen.

(6.) *Stannic chloride* (mentioned by Gmelin) will be thrown down as a yellow precipitate, gradually becoming brown on passing sulphuretted hydrogen through the acid.

(7.) *Plumbic chloride* (Vogel) may be present, derived from the lead in the sulphuric acid, as well as possibly from other sources.

(8.) *Ferric chloride* (Rose and Graham) may be recognised by neutralising the acid with sodic carbonate and afterwards adding tincture of galls or potassic ferrocyanide. With the former a violet, and with the latter a blue precipitate will be obtained.

(9.) *Other salts* may be recognised by evaporating the acid to dryness, and examining the residue.

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(10.) *Organic matter.* This is often the cause of the dark color of the acid. It may be known by evaporating the acid to dryness, and noting whether the residue becomes charred by the continued application of heat.

Preparation of Pure Hydrochloric Acid.

It will at all times be found easier to *make* a pure acid than to *purify* a bad one. The following method is recommended:—Dilute one part of good sulphuric acid with six parts of water, and pass a stream of well washed sulphuretted hydrogen through it for some hours. After allowing it to stand undisturbed for five or six days, so that any precipitate may settle, syphon off the supernatant acid, and having added a teaspoonful of common salt, concentrate by heat to the original bulk.

Fill a large retort half full of good salt, and add to it the sulphuric acid thus prepared. The retort should have fitted to it a glass tube, of such a length and shape that it may pass into a pint bottle half full of distilled water, the end of the tube dipping about $\frac{1}{8}$ of an inch under the water. The bottle is to be fitted with a second tube, connected with a second bottle of water, so that any acid vapors that escape from the water of the first bottle may be absorbed by the water of the second. The acid thus obtained will generally be found pure, but should be carefully tested before using, both by passing sulphuretted hydrogen through it, as well as by boiling with copper, the purity of which has been already proved by analysis.

Characters of pure hydrochloric acid:—

(1.) The absence of color (freedom from organic matter).

(2.) The absence of residue on evaporation to dryness (freedom from metallic salts, etc.).

(3.) No precipitate on the addition of an excess of ammonia (freedom from iron).

(4.) No precipitate with sulphuretted hydrogen (freedom from arsenic, sulphurous acid).

(5.) No precipitate in a dilute solution with baric chloride (freedom from sulphuric acid).

Hydrobromic Acid (HBr) (*Anhydrous*).

Molecular weight, 81. *Relative weight*, 40·5. *Molecular volume*, [|]. *Specific gravity*, 2·75.

Synonym.—*Hydric Bromide.*

History.—Discovered by Balard in 1826.

Preparation.—By the direct union of hydrogen and bromine vapor:—

(1.) By burning hydrogen in a mixture of air and bromine vapor. Also by combining hydrogen and bromine vapor by means of electric

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sparks, or by the contact of heated platinum, or by passage through a red hot tube ($H_2 + Br_2 = 2HBr$).

(2.) By heating potassic or sodic bromide with phosphoric acid.

[N.B.—If sulphuric acid be used instead of phosphoric acid the liberated hydrobromic acid both decomposes and is decomposed by the sulphuric acid, sulphurous acid and bromine being liberated ($2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O$)].

$$3KBr + H_3PO_4 = K_3PO_4 + 3HBr.$$

Potassic bromide + Phosphoric acid = Potassic phosphate + Hydrobromic acid.

$$[3KBr + \mathbf{P}OHo_3 = \mathbf{P}OKo_3 + 3HBr.]$$

(3.) By distilling together bromine water and phosphorus. (In this reaction a phosphorous tribromide (PBr_3) is first formed).

$$6H_2O + 3Br_2 + P_2 = 6HBr + 2(H_2PHO_3).$$

Water + Bromine + Phosphorus = Hydrobromic acid + Phosphorous acid.

$$[6\mathbf{O}H_2 + 3Br_2 + P_2 = 6HBr + 2\mathbf{P}OHHo_2].$$

A solution of the gas may be prepared—

(4.) By passing sulphuretted hydrogen through bromine water—

$$2H_2S + 2Br_2 = 4HBr + S_2.$$

Sulphuretted hydrogen. + Bromine = Hydrobromic acid + Sulphur.

$$[2\mathbf{S}H_2 + 2Br_2 = 4HBr + S_2].$$

Properties.—(α.) *Sensible and Physiological.* Hydrobromic acid is a colorless gas, having a pungent odor and an acrid acid taste. It is irrespirable, producing, even when very dilute, intense pulmonic irritation.

(β.) *Physical.* Specific gravity 2·75. It is not decomposed by heat. It may be condensed at — 92·2° F. (— 69° C.) to a liquid, and at a still lower temperature to a solid. It is freely soluble in water (*see below*).

(γ.) *Chemical.* It reddens litmus. It neither burns nor supports combustion. It fumes in the air with the liberation of a trace of bromine. Most metals are acted upon by it;—thus potassium instantly decomposes it with the liberation of hydrogen. Like hydrochloric acid it is decomposed by metallic peroxides, and by high oxygen acids. It is also decomposed by chlorine ($2HBr + Cl_2 = 2HCl + Br_2$).

Hydrobromic Acid ($HBr(H_2O)_n$) (*Solution*).

This is a solution of the gas in water. The strongest solution $HBr,5H_2O$ (containing 48·17 of HBr) has a specific gravity of 1·49, and boils at 258·8° F. (126° C.). It may be distilled without change. It fumes when exposed to the air.

Hydriodic Acid (HI) (*Anhydrous*).

Molecular weight, 128. *Relative weight*, 64. *Specific gravity* 4·4. *Molecular volume* $\boxed{|\ |}$.

Synonym.—*Hydric Iodide.*

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History.—Discovered by Guy Lussac and Davy in 1814.

Preparation.—(N.B.—Compare the similarity in the preparation of hydriodic and hydrobromic acids.)

(1.) By the *direct union* of hydrogen and iodine vapor by their passage over spongy platinum, or through a red hot tube ($H_2+I_2=2HI$).

(2.) By heating together potassic iodide (or any other iodide) and phosphoric acid :—

$$3KI + H_3PO_4 = 3HI + K_3PO_4.$$

Potassic iodide + Phosphoric acid = Hydriodic acid + Potassic phosphate.

$$[3KI + \mathbf{P}OHo_3 = 3HI + \mathbf{P}OKo_3.$$

(3.) By distilling together iodine, water and phosphorus. (In this reaction a phosphorous triiodide (PI_3) is first formed) :—

$$6H_2O + 3I_2 + P_2 = 6HI + 2H_3PO_3.$$

Water + Iodine + Phosphorus = Hydriodic acid + Phosphorous acid.

$$[6\mathbf{O}H_2 + 3I_2 + P_2 = 6HI + 2\mathbf{P}OHHo_2.]$$

(4.) By heating a mixture of phosphorus, iodine, potassic iodide and water. This reaction occurs in two stages :—

(α) Phosphoric acid and hydriodic acid are formed—

$$8H_2O + 5I_2 + P_2 = 10HI + 2H_3PO_4.$$

Water + Iodine + Phosphorus = Hydriodic acid + Phosphoric acid.

$$[8\mathbf{O}H_2 + 5I_2 + P_2 = 10HI + 2\mathbf{P}OHo_3.]$$

(β.) The potassic iodide is then acted upon by the phosphoric acid, whereby a further quantity of HI is formed :—

$$4KI + 2H_3PO_4 = 4HI + 2K_2HPO_4.$$

Potassic iodide + Phosphoric acid = Hydriodic acid + Hydric potassic phosphate.

$$[4KI + 2\mathbf{P}OHo_3 = 4HI + 2\mathbf{P}OHoKo_2.]$$

A solution of the gas may be prepared as follows :—

(5.) By passing sulphuretted hydrogen through iodine suspended in water—

$$2H_2S + 2I_2 = 4HI + S_2.$$

Sulphuretted hydrogen + Iodine = Hydriodic acid + Sulphur.

$$[2\mathbf{S}H_2 + 2I_2 = 4HI + S_2.]$$

On distillation pure hydriodic acid may be obtained.

Properties.—(α.) *Sensible and Physiological.* Hydriodic acid is a colorless gas, having a strong odor and taste. It is quite irrespirable.

(β.) *Physical.* Specific gravity 4·4. It may be liquefied by pressure; by a cold of —60° F. (—51° C.) it solidifies to an ice-like mass. It is decomposed by heat and electricity. It is very soluble in water.

(γ.) *Chemical.* Hydriodic acid reddens litmus. It neither burns nor supports combustion. It is decomposed by chlorine, by bromine and by sulphurous acid, iodine being set free ((α.) $2HI+Cl_2=2HCl+I_2$. (β.) $4HI+SO_2=2H_2O+S+2I_2$). The gas fumes in the air, the atmospheric oxygen slowly effecting its complete decomposition ($4HI+O_2=2H_2O+2I_2$). For this reason hydriodic acid is a powerful *reducing* agent, even to the conversion of sulphuric acid into sulphuretted hydrogen ($H_2SO_4+8HI=H_2S+4H_2O+4I_2$). It is decomposed

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by most metals, hydrogen being set free ($2HI+2Hg=Hg_2I_2+H_2$). With most oxides and other salts it forms iodides.

Hydriodic Acid ($HI(H_2O)_n$) (*Solution*).

This is a solution of the gas in water. The strongest solution ($2HI, 11H_2O$) has a specific gravity of 1·7, and distils unchanged at 261° F. (127° C.). It dissolves iodine, and is decomposed by atmospheric oxygen, the iodine being deposited in fine crystals. The reactions of the gas given above apply equally to its reactions in solution.

Hydrofluoric Acid (HF) (*Anhydrous*).

Molecular weight, 20. *Molecular volume*, | ' ' |. *Relative weight*, 10. *Specific gravity of vapor* 0·689; *of liquid* at 55° F. (12·8° C.), 0·987.

Synonym.—*Hydric fluoride.*

History.—Discovered by Scheele (1772). Examined and described by Guy Lussac and Thénard in 1810.

Properties.—(α.) *Physical.* The anhydrous acid is a colorless fuming liquid, which boils at about 65° F. (18·3° C.), and has a specific gravity of 0·987 at 55° F. (12·8° C.). It does not solidify at —30° F. (—34·5° C.). This anhydrous liquid acid is said to have no action on glass or on the metals, except on sodium and potassium. It chars organic substances, burns the skin, and explodes when mixed with oil of turpentine.

Hydrofluoric Acid ($HF(H_2O)_n$) (*Solution*).

This consists of a solution of the anhydrous acid in water, with which it combines with intense avidity.

Preparation.—By heating together calcic fluoride and sulphuric acid in a lead or platinum retort, and condensing the distillate in a receiver surrounded by a freezing mixture.

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4.$$

Calcic fluoride + Sulphuric acid = Hydrofluoric acid + Calcic sulphate.

$$\mathbf{Ca}F_2 + \mathbf{S}O_2Ho_2 = 2HF + \mathbf{S}O_2Cao''.$$

Properties.—(α.) *Physical.* A colorless, strongly corrosive liquid. The concentrated acid has a specific gravity of 1·060, which by sufficient dilution to form the acid $HF,2H_2O$, rises to a specific gravity of 1·150, but decreases by further dilution. The acid $HF,2H_2O$ boils at 248° F. (120° C.), and distils unchanged.

(β.) *Chemical.*—The acid fumes in the air from its affinity for water. It reddens litmus. It acts powerfully on all organic substances, explodes when mixed with turpentine, and dissolves most metals (except Au, Pt, Ag, Hg, Pb, and Mg) evolving hydrogen, and forming metallic oxides. It dissolves glass, forming a fluoride of silicon

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(SiF_4), and must therefore be preserved in gutta-percha bottles. It is not decomposed by chlorine.

Test.—Its corrosive action on glass.

General Review of the Compounds of Hydrogen and the Haloids.

(1.) **Constitution.**—They are all formed by the combination of 1 volume of hydrogen and 1 volume of the haloid element combined without condensation.

(2.) **Natural History.**—None have been found in nature in a free state, except hydrochloric acid, a trace of which has been noted in the atmosphere in the neighbourhood of volcanoes.

(3.) **Preparation.**—HCl and HF are prepared by the action of H_2SO_4 on a chloride or fluoride. HBr and HI are prepared by the action of phosphorus on the haloid element in the presence of water, a teriodide (PI_3), or a terbromide (PBr_3) being first formed, which is afterwards decomposed by the water—

$$\left.\begin{matrix}PI_3\\PBr_3\end{matrix}\right\} + 3H_2O = \left.\begin{matrix}3HI\\3HBr\end{matrix}\right\} + H_2PHO_3.$$

(4.) **Properties.**—(α.) *Sensible and physiological.* They are all colorless gases, having pungent odors, and producing excessive irritation when breathed. (β.) *Physical.* Their specific gravities vary. They may all be condensed by cold and pressure, and decomposed by heat and electricity. They are all soluble in water, forming the liquid acid. (γ.) *Chemical.* They are all acid to litmus, are non-combustible and non-supporters of combustion, are decomposed by nitric acid, are attacked by metallic peroxides, and combine with bases to form salts.

Compounds of Hydrogen and Nitrogen.

Theoretically there are four compounds of nitrogen and hydrogen, viz.:—

Imidogen (Laurent)	NH.
Amidogen (Kane and Dumas)	NH_2.
Ammonia (all chemists)	NH_3.
Ammonium (Berzelius)	NH_4.

Only one of these compounds, however, viz., ammonia, has been obtained in a free state.

Imidogen (NH).—The Imides.

The imaginary radical Imidogen is supposed to exist in certain conjugate bodies, termed by Laurent '*The Imides.*' They are not a numerous class, and are obtained by the action of heat on certain acid salts of ammonia, two molecules of water being thereby liberated. Thus $C_{10}H_{14}O_2$,NH represents camphor imide, and is formed by abstracting two molecules of water from the bicamphorate of ammonia ($NH_4HC_{10}H_{14}O_4$).

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Amidogen (NH_2).—The Amides.

Amidogen is regarded as the radical of a compound, where one hydrogen atom of ammonia has been replaced by a metal or by a compound radical. Thus, if potassium be heated in dry ammonia-gas, hydrogen is liberated, and potassic amide KH_2N is formed; or if ammonic oxalate $[(NH_4)_2C_2O_4]$ be heated, two water molecules are evolved, and oxamide $(NH_2)_2\ C_2O_2$ is left.

Two views have been entertained as to the constitution of the amides. Some regard them (1) as compounds of amidogen (NH_2) with a metal or a compound radical, and others (2) as an ammonia, where a metal or a compound group has been substituted for a hydrogen atom.

Ammonia, NH_3.

Molecular weight 17. *Molecular volume* [|]. *Relative weight* 8·5. *Specific gravity*, 0·59. *Melting point* —103° F. (—75° C.). *Boiling Point*, —37° F. (—38° C.).

Synonyms.—*Volatile Alkali; Spirit of Urine; Spirit of Hartshorn; Alkaline Air* (Priestley).

History.—Mentioned by Pliny. It was first described accurately by Black (1756), and afterwards experimented upon by Priestley (1790).

Natural History.—It is found (*α.*) In the *mineral* kingdom in air (1 in 28 million volumes (Ville)), in water and in the soil; and (*β.*) in the *organic* kingdoms in various secretions, as in the urine, etc.

Preparation.—(1.) By the action of nascent hydrogen on nitrogen; as, *e.g.*—

(*α.*) By decomposing water containing air in solution by means of a battery or with certain metals, such as iron, zinc, etc.

[Iron in rusting decomposes the moisture of the air, the free hydrogen of which combines with atmospheric nitrogen. Hence in all rust a certain amount of ammonia is to be found.]

(*β.*) By liberating hydrogen in the presence of nitrates or nitric acid ($HNO_3+4H_2=NH_3+H_2O+2H_2O$) by such means as the following:—

(i.) By acting on a solution of a nitrate with metallic aluminium and caustic soda. (Schultze).

(ii.) By acting on a solution of a nitrate with zinc and hydrochloric acid or dilute sulphuric acid ($HNO_3+4H_2=NH_3+3H_2O$).

(iii.) If nitric oxide be passed over a mixture of lime and potassic hydrate, calcic and potassic nitrates are formed together with ammonia. Similarly if nitric oxide and hydrogen be passed over warm platinised asbestos, water and ammonia are found.

(2.) By the decomposition of organic matters containing nitrogen.

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This may be—

(α.) *Spontaneous*, as when organic matter decays; or

(β.) The result of *destructive distillation;* as *e.g.*, by heating horn, coal, etc., in closed retorts. Thus, most of the commercial ammonia salts are derived from the ammoniacal liquor produced during the distillation of coal.

(NOTE.—The nitrogen of all nitrogenised bodies (provided it be not present as a nitrate or cyanide) is evolved as ammonia when heated with the hydrated alkalies.)

(γ.) By acting on ammoniacal salts with an alkali or alkaline earth.

$$2\mathbf{N}H_4Cl + \mathbf{Ca}O = \mathbf{Ca}Cl_2 + 2\mathbf{N}H_3 + \mathbf{O}H_2.$$

Ammonic chloride + Lime = Calcic chloride + Ammonia + Water.

Properties.—(α.) *Sensible and physiological.* A colorless gas, having a pungent odor, and an acrid taste. When the concentrated gas is inhaled it is poisonous, but when dilute its action is stimulating.

(β.) *Physical.* The specific gravity of ammonia gas is 0·59. By a cold of —40° F. (—40 °C.), or by a pressure of 6 atmospheres at 50° F. (10° C.), or of 8·5 atmospheres at 68° F. (20° C.), the gas is condensed into a clear, mobile, highly refractive, liquid, which boils at —37° F. (—38° C.). The liquid ammonia dissolves sulphur, phosphorus, iodine, and the alkaline metals, forming with these last a blue solution, from which the metal is deposited unchanged when the ammonia is evaporated. At a cold of —103° F. (—75° C.), the liquid ammonia freezes to an ice-like solid, having a greater specific gravity than the liquid.

In "*Carré's ice making apparatus*" liquid ammonia is first formed by condensing ammonia gas into a liquid in a strong iron vessel, which liquid, in again becoming a gas, absorbs so much heat that it freezes the water with which the liquid ammonia is surrounded.

Ammonia gas may be decomposed either by electric sparks or by passing it through a hot porcelain tube. In each case the volume of gas formed is double the original volume operated on. Ammonia gas is very readily absorbed by clayey and peaty soils, by most porous bodies, by water (more freely indeed than any other gas), and by alcohol. No definite combination of water and ammonia is believed to occur, the absorption being a merely physical act of solution.

(γ.) *Chemical.* Ammonia has an alkaline reaction; turmeric is turned brown by it, and red litmus blue, but the changes are not permanent (volatile alkali). It is not a supporter of combustion, and is very feebly combustible, burning under favorable conditions with a greenish yellow flame, water and free nitrogen forming the products.

Action of oxygen. When 3 to 4 parts of ammonia gas are mixed with 1 part of oxygen it explodes, water, nitrogen, and traces of nitric acid being formed. If ozonized air be mixed with ammonia gas, white clouds of ammonic nitrite are formed from the ammonia becoming oxidised to nitrous acid ($4NH_3 + 3O_2 = 2(NH_4,NO_2) + 2H_2O$).

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This oxidation of ammonia may also be effected by a hot platinum wire introduced into a mixture of the gas and air. In the presence of a strong base, the oxidation of ammonia to nitric acid, and its subsequent combination with the base, constitutes a process termed *nitrification* ($2NH_3 + K_2O + 4O_2 = 2KNO_3 + 3H_2O$).

Action of the haloids.—Ammonia is decomposed by chlorine with the formation of the hydrogen acid ($8NH_3 + 3Cl_2 = 6NH_4Cl + N_2$). With *acids*, ammonia forms salts. Thus when the volatile hydrochloric acid is brought near ammonia, white fumes of ammonic chloride are produced, a reaction constituting a test for the presence of the alkali. Neither the *alkalies*, nor the *combustible* solids have any action upon it.

Action on metallic salts.—Ammonia combines with various metallic salts, at times apparently taking the place of their water of crystallisation, but not necessarily analogous, so far as the relationship between the number of the molecules is concerned. Thus, cupric sulphate has the formula $CuSO_4,5H_2O$, and ammoniated cupric sulphate the formula $CuSO_4,4H_3N,H_2O$. Hence ammonia frequently acts on metallic salts differentiy to potassic or sodic hydrate. (α.) If the ammonia be in *insufficient quantity* to neutralise the acid, a basic salt may be precipitated ($4CuSO_4 + 6H_3N + 7H_2O = 3(H_4N)_2SO_4 + CuSO_4,3CuO,4H_2O$); or ($\beta$.) If it be added *in excess* a precipitate may be formed either of the hydrated metallic oxide, together with an ammonic salt ($2Fe_23SO_4 + 12H_3N + 9H_2O = 6(H_4N)_2SO_4 + 2Fe_2O_3,3H_2O$), or of a combination of ammonia with the precipitated oxide [as *e.g.*, uranic oxide, forming $(H_4N)_2O,2U_2O_3$], or of a double salt of the metal and ammonium, as *e.g.*, the ammonic magnesic phosphate $(H_4N)_2Mg_2P_2O_8$, $12H_2O$), or various ammoniated salts may be formed, such as the ammoniated cupric sulphate, or various substitution products may result, where one or more atoms of hydrogen are replaced by a metal or by an electro-positive radical. Thus :—

Potass-amine	NH_2K.
Tri-chlor-amine	NCl_3 (?).
Tri-zinc-amine	NZn_3.
Platin-amine	N_2H_4Pt''
Ethyl-amine	$NH_2(C_2H_5)$.
Di-ethyl-amine	$NH(C_2H_5)_2$.
Tri-ethyl-amine	$N(C_2H_5)_3$.
Acet-amine	$NH_2(C_2H_3O)$.
Sulpho-amine	$N_2H_4(SO_2)''$.

Solution of Ammonia (Liquor Ammoniæ).—This is merely a solution of the gas in water.

At 32° F. (0°C.) water absorbs 1050 vols. of NH_3.
At 59° F. (15° C.) ,, ,, 727 ,, ,, ,,
At 77° F. (25° C.) ,, ,, 586 ,, ,, ,,

When these solutions are boiled the whole of the ammonia is evolved.

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The specific gravity of the solution of ammonia varies with its strength. (See Table IV. in Appendix.)

Ammonia solution is a colorless, alkaline liquid, having a very caustic taste, and blistering the skin. It freezes at —40° F. (—40° C.) The gas is evolved at ordinary temperatures. The solution dissolves many salts (as AgCl) and oxides (CuO, ZnO, Ag_2O) that are insoluble in water.

If the liquid be pure it should on evaporation leave no residue.

The impurities of a solution of ammonia are—

(α.) *Carbonic acid.—Test:* White precipitate with lime water.

(β.) *Chlorine.—Test:* White precipitate on adding argentic nitrate to the solution neutralised with nitric acid.

(γ.) *Sulphuric acid.—Test:* White precipitate on adding baric nitrate to a solution neutralised with nitric acid.

(δ.) *Lime—Test*: White precipitate with ammonic oxalate.

(ε.) *Lead or copper* (derived from the apparatus, or from the solution having been kept in glass containing lead).—*Test:* Brown or black precipitate with sulphuretted hydrogen.

Ammonium (NH_4).

This compound metal has never been isolated. Its possible existence has been inferred by the close relationship of the ammonium salts to those of sodium and potassium, and also by the production of an amalgam having the metallic lustre of ordinary amalgams, under circumstances where its formation is theoretically possible. This amalgam rapidly decomposes into mercury, ammonia and hydrogen.

The amalgam may be prepared as follows:—

(1.) By placing a globule of mercury connected with the negative pole of a battery on a piece of moistened sal ammoniac (NH_4Cl) placed on a piece of platinum foil, and connected with the positive pole.

(2.) By pouring a little potassic amalgam into a saturated solution of sal-ammoniac, when the amalgam rapidly swells up, potassic chloride being formed at the same time.

Compounds of Hydrogen with Phosphorus.

1. *Gaseous* phosphoretted hydrogen PH_3 ($\mathbf{P}H_3$).
2. *Liquid* phosphoretted hydrogen...PH_2 or P_2H_4 ($\mathbf{P}_2H_4$).
3. *Solid* phosphoretted hydrogen ...P_2H or P_4H_2 $\left\{\begin{matrix}\mathbf{P}(P'''H)''\\ \mathbf{P}(P'''H)''\end{matrix}\right.$ (?)

None of these can be easily prepared by direct union.

Gaseous Phosphoretted Hydrogen, PH_3 ($\mathbf{P}H_3$.)

Molecular weight, 34. *Molecular volume*, $\boxed{\ |\ |\ }$. *Relative weight*, 17. *Specific gravity*, 1·19.

Synonyms.—*Phosphamine* (from its analogy to ammonia); *Phosphorous Trihydride.*

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History.—Discovered by Guigembre (1783), whilst distilling potash with spirit that had been used for anatomical preparations. It was afterwards studied by Davy (1812), who devised other methods for its preparation, and also by Dumas, Rose, etc.

Natural History.—Evolved during the decomposition of phosphorised organic bodies (odor of fish).

Preparation.—(1.) By heating phosphorous or hypophosphorous acids.

(α.) $4H_3PO_3 = PH_3 + 3H_3PO_4$.
Phosphorous acid = Phosphoretted hydrogen + Phosphoric acid.
[$4\mathbf{P}OHHo_2 = \mathbf{P}H_3 + 3\mathbf{P}OHo_3$].

(β.) $2H_3PO_2 = PH_3 + H_3PO_4$.
Hypophosphorous acid = Phosphoretted hydrogen + Phosphoric acid.
[$2\mathbf{P}OH_2Ho = \mathbf{P}H_3 + \mathbf{P}OHo_3$].

(2.) By boiling phosphorus in a strong solution of an alkali or an alkaline earth.

$3KHO + P_4 + 3H_2O = 3KPH_2O_2 + PH_3$.
Potassic hydrate + Phosphorus + Water = Sodic hypophosphite + Phosphoretted hydrogen.
[$3\mathbf{O}KH + P_4 + 3\mathbf{O}H_2 = 3\mathbf{P}OH_2Nao + \mathbf{P}H_3$].

[N.B.—(α.) Free *hydrogen* is also evolved by the action of an excess of free alkali on the hypophosphite, a phosphate being formed as well as the liquid PH_2.

(β.) If alcohol be used instead of water the non-inflammable form is generated.]

(3.) By decomposing calcic phosphide (prepared by passing phosphorus vapor over red hot lime) with water.

(4.) By the action either of water or potassic hydrate on phosphoric iodide.

(α.) $PH_4I = HI + PH_3$.

(β.) $PH_4I + KHO = PH_3 + KI + H_2O$.

[N.B.—This PH_3 is not inflammable.]

(5.) Possibly it is produced in very small quantities by the action of nascent hydrogen on phosphorus.

Properties.—(α.) *Sensible and physical.* A colorless, stinking gas. Specific gravity 1·19. It may be liquefied by pressure, and is decomposed by heat and electricity. Water absorbs from one-fourth to one-fiftieth of its volume.

(β.) *Chemical.* Although in constitution analogous to ammonia, it has no alkaline reaction, but is, on the contrary, feebly acid to blue litmus. Nevertheless its analogy to ammonia is shown by its combining with certain acids, such as hydriodic and hydrobromic acids, forming with them the crystalline compounds *phosphoric iodide* (PH_4I) and *phosphoric bromide* (PH_4Br). Both of these compounds are decomposed by water. The gas as ordinarily prepared is spontaneously inflammable; but this is not the case with the pure gas. This spon-

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taneous inflammability depends on the presence of a trace of the vapor of *liquid* phosphoretted hydrogen (PH_2), one part of which in 500 of PH_3 is sufficient to confer this property upon it. (1.) *The pure non-inflammable gas may be rendered inflammable* (α.) by mixing it with a little PH_2 vapor; or (β.) by bubbling it through nitric acid containg nitrous acid in solution, $\frac{1}{10,000}$th part of its bulk of nitrous anhydride being sufficient for this purpose. Or again, (2,) *The spontaneously inflammable gas may be rendered non-inflammable* (α) by passing it over charcoal; or (β) by exposing it to sunlight, or (γ) by passing it through hydrochloric acid; in both of which latter cases the liquid phosphoretted hydrogen is decomposed into solid and gaseous phosphoretted hydrogen ($5PH_2 = P_2H + 3PH_3$), or (δ) by exposing the gas to a freezing mixture, whereby the vapor of the liquid phosphoretted hydrogen is condensed, or lastly (ϵ) by mixing it with certain vapors, such as those of ether, turpentine, alcohol, etc. When the impure gas is ignited it produces wreaths of white smoke, due to the formation of phosphoric anhydride. The gas explodes when mixed with oxygen. The haloids, sulphurous acid and some of the metals decompose it. It is mostly decomposed when passed into metallic solutions, phosphides of the metals being precipitated ($3CuSO_4 + 2PH_3 = 3H_2SO_4 + P_2Cu_3$). In the case of gold and silver salts the metals are reduced, phosphoric acid remaining in solution.

Liquid Phosphoretted Hydrogen, P_2H_4 $\left\{\begin{matrix}\mathbf{P}H_2\\ \mathbf{P}H_2\end{matrix}\right.$

Preparation.—By passing phosphoretted hydrogen (prepared by the action of water on calcic phosphide) through a freezing mixture.

Properties.—A light yellow liquid, boiling at 95° F. (35° C.), not solidifying at —4° F. (—20° C.), very inflammable, and decomposed by sunlight into solid and gaseous phosphoretted hydrogen ($5P_2H_4 = 6PH_3 + P_4H_2$). It fires on exposure to air. The presence of this body in gaseous phosphoretted hydrogen confers on it the property of spontaneous inflammability (Thénard.) A similar effect is produced by its admixture with hydrogen, with carbonic oxide, or with other combustible gases.

Solid Phosphoretted Hydrogen, P_4H_2 $\left\{\begin{matrix}\mathbf{P}(P'''H)''\\ \mathbf{P}(P'''H)''\end{matrix}\right.$

Preparation.—By the action of sunlight or of hydrochloric acid on liquid phosphoretted hydrogen, or by the action of hydrochloric acid on calcic phosphide.

Properties.—A yellow solid, firing at 302° F. (150° C.), insoluble in water or in alcohol, but soluble in a solution of potassic hydrate, gaseous phosphoretted hydrogen being evolved.

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COMPOUNDS OF HYDROGEN AND SULPHUR.

Sulphuretted hydrogen	H_2S.
Persulphuretted hydrogen	H_2S_2 (?).

Sulphuretted Hydrogen, H_2S (SH_2).

Molecular weight, 34. *Molecular volume*, [ ]. *Relative weight*, 17. *Specific gravity*, 1·1912.

Synonyms.—*Dihydric sulphide; Hepatic air; Hydrogen monosulphide; Sulphidic acid; Hydrosulphuric acid.*

History.—Discovered by Scheele (1777).

Natural History.—(α.) In the *mineral* kingdom, sulphuretted hydrogen is found in the gases issuing from volcanoes, often to the extent of 25 per cent.

It is found in certain mineral *waters*, as, *e.g.*, in those of Harrogate, Aix-la-Chapelle, etc., and in the sea-water near the mouths of rivers. The water on the west coast of Africa is stated to contain 6 cubic inches of sulphuretted hydrogen per gallon, the smell of the gas being noticeable 27 miles out at sea. In these cases the conditions of its formation are the presence in the water of organic matter and of sulphates, the former being oxidized by the oxygen of the latter, until a sulphide is formed ($CaSO_4 - O_4 = CaS$). When this sulphide is acted on by the carbonic acid in the water, sulphuretted hydrogen is set free ($CaS + H_2O + CO_2 = CaCO_3 + H_2S$). The unpleasant taste of many aerated waters is due to their having been manufactured with water containing organic matter and sulphates, whereby a sulphide is formed, which is decomposed by the carbonic acid present in large excess.

Its presence in sewer-gas results from the putrefaction of organic matters containing sulphur, as well as by the process already described. In the neighbourhood of sulphate of ammonia works, it may often be detected in the air, for in distilling coal (as well as in the destructive distillation of all organic matters containing sulphur) large quantities of the gas are generated, which, combining with the ammonia, collect in the ammoniacal liquor. It is also set free in quenching the coke at the gas works, the hydrogen of the decomposed water combining with the sulphur of the fuel. Large quantities of H_2S are also evolved in the last part of the process of tar distillation. It may be worth noting here that if present in a room it may be entirely removed by setting free a trace of chlorine.

(β.) In the *vegetable* kingdom it is unknown, whilst (γ) in the *animal* kingdom it is found in intestinal flatus, and in decomposing animal matters.

Preparation.—(1.) By the *direct union* of hydrogen and sulphur. (α.) By heating together sulphur and hydrogen; or (β) by passing hydrogen into boiling sulphur; or (γ) by burning hydrogen in

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sulphur vapor or sulphur vapor in hydrogen; or (δ) by passing steam and sulphur vapor through a tube filled with red hot pumice stone.

(2.) By decomposing a metallic sulphide with an acid; *e.g.* :—

(α.) Dilute sulphuric acid on ferrous sulphide—

H_2SO_4 + FeS = $FeSO_4$ + H_2S.

Sulphuric acid + Ferrous sulphide = Ferrous sulphate + Sulphuretted hydrogen.

[$\mathbf{S}O_2Ho_2$ + $\mathbf{Fe}S''$ = $\mathbf{S}O_2Fe o''$ + $\mathbf{S}H_2$.]

(β.) Dilute hydrochloric acid on antimonious sulphide:—

6HCl + Sb_2S_3 = $2SbCl_3$ + $3H_2S$.

Hydrochloric acid + Antimonious sulphide = Antimonious chloride + Sulphuretted hydrogen.

[6HCl + $\mathbf{Sb}_2S_3$ = $2\mathbf{Sb}Cl_3$ + $3\mathbf{S}H_2$.]

Properties.—(α.) *Sensible and physiological.* Sulphuretted hydrogen is a colorless gas, having the odor of rotten eggs. Physiologically, it acts as a narcotic, and is very poisonous; 1 part in 1,500 will kill birds; 1 in 1,000, dogs; 1 in 250, horses. (Dupuytren and Thénard.)

(β.) *Physical.* Its specific gravity is 1·1912. 100 cubic inches weigh 38 grains, and 1 litre 1·51991 grms. By a pressure of seventeen atmospheres, or by a cold of —101° F. (—74° C.), it may be condensed into a colorless liquid, which boils at —79·6° F. (—62° C.), and freezes at —122·8° F. (—86° C.). It is decomposed both by heat and electricity. Water freely absorbs it; at 32° F. (0° C.), it dissolves 4·37 times its bulk of the gas; at 59° F. (15° C.) 3·23 times, and at 75° F. (24° C.) 2·66 times.

(γ.) *Chemical.* Sulphuretted hydrogen reddens litmus feebly. It is a combustible gas. If the supply of air be free, water, sulphurous acid, with a little sulphuric acid (if the air be moist), are formed. If the supply of air be limited, sulphur is deposited. It will be noted, therefore, that any sulphuretted hydrogen evolved in manufacturing operations, may be effectually removed by passing the gas through the furnace.

Mixed with *oxygen* in the proportion of 1 part of H_2S to 1·5 of O, it explodes on the application of heat. By the action of the *haloid elements*, sulphuretted hydrogen is immediately decomposed, the haloid appropriating the hydrogen and liberating sulphur ($SH_2 + Cl_2 = 2HCl + S$). *Oxy-acids* (such as nitric, sulphurous acids, etc.), decompose it, setting free sulphur. It is absorbed by the *alkalies*, forming sulphides (*as* K_2S), solutions of which, on being further treated with sulphuretted hydrogen, form sulphydrates or hydrosulphides ($K_2S + H_2S = 2KHS$).

Certain *metals* displace hydrogen from the gas, forming a sulphide. This occurs in some cases at *ordinary temperatures* (as *e. g.*, in the case of Hg, Ag, etc.), ($Hg_2 + H_2S = Hg_2S + H_2$). Thus, silver is blackened by exposure to the air of towns, a silver spoon by the sulphur of an egg, and silver coins by keeping them with sulphur matches in the pocket. [The black sulphide thus formed may be removed by strong

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ammonia or by potassic cyanide.] In other cases, *heat* is required to effect combination (as *e. g.*, in the case of K, Sn, etc.)

(α.) $2H_2S+K_2=2KHS+H_2$. (β.) $H_2S+Sn=SnS+H_2$.

In this latter case it will be remarked that the volume of hydrogen evolved is identical with the volume of sulphuretted hydrogen operated upon. *Metallic oxides* are changed, by the action of the gas, into their corresponding sulphides, water being formed simultaneously ($PbO+H_2S=PbS+H_2O$). A similar action is observed in the case of the metallic salts ($Pb(NO_3)_2+H_2S=2HNO_3+PbS$). Thus, the lead used for paint becomes black, although the black sulphide (PbS) formed is, under the influence of air and light, converted into the white sulphate ($PbSO_4$). The colors of the various sulphides produced when the gas is passed through metallic solutions are, in many cases, very characteristic, and constitute important tests. On *metallic chlorides* the action of the gas is similar to that on oxides.

The solution of sulphuretted hydrogen has a feebly acid reaction. It rapidly decomposes, becoming turbid, from the atmospheric oxygen combining with the hydrogen, whereby sulphur (the electro-negative variety) is precipitated as a white deposit. It is better, therefore, to make the solution with water that has been well boiled, or has been previously saturated with the gas.

Uses.—In the laboratory, as a test for the metals.

Tests.—Blackens lead paper.

Persulphuretted Hydrogen (H_2S_2 ?) $'S'_2H_2$, or Hs_2.

Molecular weight, 66 (?). *Specific gravity*, 1·769.

Synonyms.—*Persulphide of hydrogen; Hydric persulphide; Dihydric disulphide; Hydrosulphyl* (Frankland).

History.—Discovered by Scheele (1777). Its properties were fully investigated by Berthollet.

Preparation.—Lime and sulphur are first boiled together, whereby a disulphide of calcium is formed ($'S'_2Ca''$). This solution is then dropped into dilute hydrochloric acid (1 of acid to 2 of water), when persulphuretted hydrogen is formed:—

CaS_2	+	2HCl	=	H_2S_2	+	$CaCl_2$.
Calcic disulphide	+	Hydrochloric acid	=	Persulphuretted hydrogen	+	Calcic chloride.
$'S'_2Ca''$	+	2HCl	=	S_2H_2	+	$CaCl_2$.

[Note.—If the acid be poured into the calcic disulphide solution, then another reaction occurs, sulphur being precipitated (sulphur præcipitata, P. B.) $CaS_2+2HCl=CaCl_2+H_2S+S$].

Properties.—(α.) *Sensible and physiological.* A yellowish oily liquid having a sulphuretted hydrogen odor. Specific gravity, 1·769. It is a very unstable body, and is decomposed by a slight heat into sul-

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phuretted hydrogen and sulphur. It is insoluble in water, but soluble in ether.

(β.) *Chemical.* Persulphuretted hydrogen is inflammable, and burns with a blue flame. Its composition is doubtful, but it is believed to be analogous to hydroxyl (H_2O_2). It is closely allied to it in certain of its reactions. Thus, it bleaches litmus. The presence of acids increase, whilst alkalies decrease its stability. It dissolves free sulphur, and is decomposed, like hydroxyl, by the mere contact of certain metals and metallic peroxides. It is believed to combine with many vegetable alkaloids.

Seleniuretted Hydrogen, H_2Se (SeH_2.)

Molecular weight, 81·5. *Molecular volume* $\boxed{\ |\ |\ }$. *Relative weight*, 40·75. *Specific gravity*, 2·8.

Synonyms.—*Selenetted hydrogen; Hydroselenic acid; Dihydric selenide; Selenhydric acid.*

History.—Discovered by Berzelius.

Preparation.—(1.) By passing hydrogen and selenium vapor through red-hot tubes.

(2.) By the action of acids on selenides :—

FeSe	+	2HCl	=	H_2Se	+	$FeCl_2$.
Ferrous selenide	+	Hydrochloric acid	=	Seleniuretted hydrogen	+	Ferrous chloride.
[**Fe**Se″	+	2HCl	=	**Se**H_2	+	**Fe**Cl_2].

Properties.—(α.) *Sensible, physical, and physiological.*—A colorless, offensive smelling gas, producing great irritation and violent nasal catarrh. Specific gravity, 2·8. Soluble in water.

(β.) *Chemical.* Inflammable. The solution in water is feebly acid. When exposed to the air it absorbs oxygen, depositing selenium. Its reactions are closely allied to those of sulphuretted hydrogen, precipitating in many cases metallic selenides when passed through solutions of metallic salts. The alkaline selenides are soluble. The selenides of zinc and manganese are coloured, but the rest are black.

Compounds of Carbon and Hydrogen.

These compounds, termed generically hydrocarbons, belong chiefly, if not entirely, to organic chemistry. Three of these compounds will be described here, viz., marsh gas, CH_4; olefiant gas, C_2H_4; and acetylene, C_2H_2. These three bodies are, moreover, the starting points of three series of hydrocarbons, the members of which, as in the case of other hydrocarbon series, increase by a regular increment, or some multiple of CH_2, such a series being termed an *homologous series*. Thus—

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Marsh Gas Series.	*Olefiant Gas Series.*	*Acetylene Series.*
$(CH_2)_n+H_2$.	$(CH_2)_n$.	$(CH_2)_n-H_2$.
Methane (marsh gas) CH_4	Ethylene (olef. gas) C_2H_4	Acetylene .. .. C_2H_2
Ethane .. .. .. C_2H_6	Propylene .. .. C_3H_6	Allylene.. .. .. C_3H_4
Propane .. .. .. C_3H_8	Butylene .. .. C_4H_8	Crotonylene .. .. C_4H_6
Etc.	Etc.	Etc.

Methane, or Light Carburetted Hydrogen, CH_4.

Molecular weight, 16. *Molecular volume* [|]. *Relative weight*, 8. *Specific gravity*, 0·5576.

Synonyms.—*Marsh gas; Methane; Methylic hydride* (CH_3H); *Sub-carburetted hydrogen; Heavy inflammable air; Fire damp; Pit gas.*

History.—First examined by Volta (1778).

Natural History.—Found in stagnant ditches, *i.e.*, wherever vegetable matter is decomposing out of contact with air, but in the presence of moisture (marsh gas). It occurs occluded in coal, 100 grains of which will at times yield 200 c.c. of gas, containing nearly 90 per cent. of marsh gas, the remaining 10 per cent. consisting of nitrogen, oxygen, and carbonic acid. It is evolved from the earth in many volcanic districts.

Preparation.—(1.) By the decomposition of organic matter (as sewage) out of contact with air.

(2.) By the dry distillation of coal.

[Probably CH_4 and CO_2 were the two gases formed when the hydrogen and oxygen were separated from the wood during its change into coal].

(3.) By heating acetic acid or an acetate, with sodic or potassic hydrate:—

$$KH_3C_2O_2 + KHO = K_2CO_3 + CH_4.$$
Potassic acetate + Potassic hydrate = Potassic carbonate + Methane.

$$\left[\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OKo\end{matrix}\right. + KHo = \mathbf{C}OKo_2 + \mathbf{C}H_4\left.\right]$$

(4.) By passing a mixture of carbonic disulphide vapor and sulphuretted hydrogen (or steam) over red-hot copper:—

$$CS_2 + 2SH_2 + 4Cu = 4CuS + CH_4$$
Carbonic disulphide + Sulphuretted hydrogen + Copper = Cupric sulphide + Methane.

$$[\mathbf{C}S_2'' + 2\mathbf{S}H_2 + 4Cu = 4\mathbf{Cu}S + \mathbf{C}H_4].$$

(5.) By the action of water on zincic methide.

$$Zn(CH_3)_2 + 2H_2O = 2CH_4 + ZnO_2H_2.$$
Zincic methide + Water = Methane + Zincic hydrate.

(6.) By the action of nascent hydrogen on chloroform ($CHCl_3$), or on CCl_4, or on CHI_3.

$$CHCl_3 + 3H_2 = CH_4 + 3HCl.$$
Chloroform + Hydrogen = Methane + Hydrochloric acid.

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Properties.—(α.) *Sensible and physiological.*—A colorless, odorless, tasteless gas. It has no injurious action on the body.

(β.) *Physical.*—Specific gravity, 0·5576. It possesses great powers of diffusion. It cannot be condensed by cold or pressure. It may, although with difficulty, be completely decomposed by heat and electricity, carbon being deposited, and a double volume of hydrogen evolved. Passed through a red-hot tube, hydrogen, ethylene, acetylene, and ethylic hydride are formed. 100 volumes at 32° F. (0° C.) absorb about 5·4 volumes of the gas.

(γ.) *Chemical.*—It is a very inert gas, and constitutes the first member of the *paraffin* series (*parum* and *affinitatis*). It has no action on turmeric or on litmus. It contains more hydrogen than any other compound of C and H. It burns with a pale illuminating flame, a white heat or actual flame being required for its ignition, carbonic anhydride and water constituting, if the supply of air be free, the products of its combustion, whilst acetylene and other products are formed if the supply be limited. Exploded with *twice* its volume of oxygen, carbonic anhydride and water result, whilst with 1·5 times its volume, carbonic oxide and water are formed. It explodes even when mixed with air in the proportion of 1 part of the gas to 17 of air, the energy of the explosion increasing until the methane constitutes one-seventh of the total volume.

Action of the Haloids.—Iodine and bromine, are without action upon it. Chlorine does not combine with it in the dark, whilst in sunlight the union is intensely energetic, forming, in the presence of moisture, carbonic anhydride and hydrochloric acid ($CH_4+4Cl_2+2H_2O=CO_2+8HCl$). If the chlorine be present in great excess the substitution of chlorine for the hydrogen may be effected, carbonic tetrachloride, CCl_4, or lower derivatives such as $CHCl_3$,$CHCl_2$, etc., being formed.

Neither sulphur nor phosphorus, acids nor alkalies have any action on the gas.

Ethylene or Heavy Carburetted Hydrogen C_2H_4 $\left\{\begin{matrix}CH_2.\\CH_2.\end{matrix}\right.$

Molecular weight, 28. *Molecular volume*, $\square$. *Relative weight* 14. *Specific gravity* 0·978.

Synonyms. — *Olefiant gas* (Dutch chemists); *Ethylene; Elayl* (Berzelius); *Etherene* (Faraday); *Etherin.*

History.—Discovered by the associated Dutch chemists (1795). Afterwards studied by Berthollet.

Natural History.—Present to the extent of 1 to 6 per cent. in fire damp.

Preparation.—(1.) By the dry distillation of coal and other organic bodies (resins, fats, oils, etc.)

(2.) By the action of sulphuric acid (or other dehydrating agents,

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such as boric anhydride) on alcohol at a temperature of about 329° F. (165° C.) The action occurs in two stages :—

(α.) Sulphovinic acid is first formed—

$$C_2H_5(OH) + H_2SO_4 = C_2H_5,HSO_4 + H_2O.$$
Alcohol + Sulphuric acid = Sulphovinic acid + Water.

(β.) The sulphovinic acid is afterwards decomposed by heat into ethylene and sulphuric acid—

$$C_2H_5,HSO_4 = C_2H_4 + H_2SO_4.$$
Sulphovinic acid = Ethylene + Sulphuric acid.

(3.) By the action of nascent hydrogen on acetylene ($C_2H_2+H_2=C_2H_4$).

[Note.—Acetylene, C_2H_2, is the only hydrocarbon that can be prepared artificially. From it ethylene, and from ethylene, alcohol can be formed.]

Properties.—(α.) *Sensible.* A colorless, odorless gas, having an anæsthetic action.

(β.) *Physical.* Specific gravity 0·978. It may be liquefied by cold and pressure at —166° F. (—110° C.) (Faraday), but it cannot be frozen. It is decomposed by a red heat and by electric sparks. If the heat be not too great, acetylene and hydrogen are formed ($C_2H_4=C_2H_2+H_2$); at a higher temperature marsh gas is produced, and one half of the carbon is deposited ($C_2H_4=CH_4+C$), whilst at a higher temperature still, it suffers complete decomposition ($C_2H_4=C_2+2H_2$.) Water absorbs about one-eighth its bulk of the gas. Alcohol, ether, the volatile and fixed oils also dissolve it.

(γ.) *Chemical.* It has no action either on litmus or turmeric. It burns with an intense white light, constituting one of the chief illuminants of coal gas. When mixed with three volumes of oxygen, it explodes ($C_2H_4+3O_2=2CO_2+2H_2O$), water and carbonic anhydride resulting.

Action of the haloids.—(α.) When olefiant gas is fired with twice its volume of chlorine, it deposits carbon and forms hydrochloric acid. (β.) Mixed with its own volume of chlorine and exposed to diffuse light, it forms an oily body called *Dutch liquid*, $C_2H_4Cl_2$ (Dichlorethane; Ethylene chloride). This liquid has a specific gravity of 1·256 at 53·6° F. (12° C.), and boils at 183·2° F. (84° C.). The formation of this body is the origin of the name "Olefiant gas." (γ.) When the gas is mixed with a larger proportion of chlorine, and exposed to sunlight, the product C_2Cl_6 may be formed. Bromine, but not iodine, forms products of a similar kind. An *Ethylene iodide*, $C_2H_4I_2$ may be produced by passing ethylene into a mixture of iodine and absolute alcohol.

Phosphorus and sulphur have no action upon it.

Fuming sulphuric acid (or SO_3) absorbs it, forming ($C_2H_4,2SO_3$) ethyl-sulphuric acid. Mixed with an alkaline solution of potassic permanganate, carbonic, formic, and oxalic acids are produced.

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Acetylene C_2H_2 $\left\{ \begin{matrix} ''CH. \\ ''CH. \end{matrix} \right.$

Molecular weight, 26. *Molecular volume*, $\boxed{\ |\ |\ }$. *Relative weight*, 13.
Specific gravity, 0·92.

Synonyms.—*Ethine; Klumene.*

Preparation.—(1.) By the direct combination of carbon with hydrogen; as, *e. g.*, by the combustion of the carbon poles from a powerful battery in an atmosphere of hydrogen.

(2.) By the incomplete combustion of bodies containing carbon and hydrogen, such, *e. g.*, as methane, vapor of alcohol, etc.

(3.) By the action of an alcoholic solution of potassic hydrate on bromethylene—

C_2H_3Br	+	KHO	=	C_2H_2	+	KBr	+	H_2O.
Bromethylene	+	Potassic hydrate	=	Acetylene	+	Potassic bromide	+	Water.

(4.) By the electrolysis of fumaric acid ($C_2H_2(COOH)_2 = C_2H_2 + 2CO_2 + H_2$).

(5.) By passing a mixture of methane and carbonic oxide through a red hot tube ($CH_4 + CO = C_2H_2 + H_2O$).

Properties.—(α.) *Sensible.* A colorless gas, having a geranium odor. It is very poisonous.

(β.) *Physical.* Specific gravity 0·92. It has never been condensed. It is decomposed by an intense heat (such as electric sparks) with the separation of carbon. By the action upon it of a continuous red heat, benzene (C_6H_6) has been formed, together with a liquid hydro-carbon called styrole (C_8H_8), and which hitherto had only been obtained from storax. Acetylene is the most stable of all carbon compounds. It is soluble in water, the solution answering to the tests.

(γ.) *Chemical.*—It burns with a smoky flame, 1 volume of gas consuming 2·5 volumes of oxygen, and forming 2 volumes of CO_2. Mixed with chlorine and exposed to diffuse daylight, it explodes spontaneously, with the separation of carbon ($C_2H_2 + Cl_2 = C_2 + 2HCl$). It combines with bromine to form acetylene dibromide ($C_2H_2Br_2$). When electric sparks are passed through a mixture of nitrogen and acetylene, hydrocyanic acid is formed ($C_2H_2 + N_2 = 2CNH$). Oxidizing agents, such as potassic permanganate, convert it into oxalic acid. It is absorbed by sulphuric acid, with the production of vinyl-sulphuric acid ($SO_2(C_2H_3O)Ho$). It combines directly with hydrogen to form olefiant gas ($C_2H_2 + H_2 = C_2H_4$).

Tests.—(α.) With *cuprous chloride* it forms a red explosive precipitate of cuproso-vinyl oxide [cuprous acetylide or cuproso-vinylic ether, $(C_2Cu_2H)_2O$], $2Cu_2Cl_2 + 2C_2H_2 + H_2O = 4HCl + (C_2Cu_2H)_2O$. This body is supposed to have caused explosions in brass and copper

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pipes used for gas. It is immediately decomposed by hydrochloric acid, acetylene being set free ($(C_2Cu_2H)_2O + 4HCl = 2Cu_2Cl_2 + H_2O + 2C_2H_2$). By the action of nascent hydrogen it forms ethylene.

(β.) It gives a white explosive precipitate with argentic nitrate, insoluble in ammonia or in nitric acid.

Coal Gas.

Three classes of products are formed by the dry distillation of coal—gas, water, and tar, the relative proportions of each depending much on the temperature to which the coal is subjected. Coal gas is a compound gas, consisting of illuminants, diluents, and impurities. The *illuminants* are, olefiant gas (C_2H_4), and analogous hydrocarbons (C_3H_6, C_4H_8, etc.), and hydrocarbon vapors, such as the vapor of benzol. The *diluents* are, hydrogen, marsh gas, and carbonic oxide. The *impurities* are, carbonic anhydride, sulphuretted hydrogen, and other sulphur compounds.

The following table, from Roscoe, represents the composition of coal gas, prepared respectively from cannel and from common coal. In estimating the illuminating power of a gas, we compare the light given by the gas burning from a 24-hole argand, at 5 feet per hour, with a sperm candle burning at the rate of 120 grains.

	Illuminating power compared to sperm candle burning 120 grains per hour, the gas burning 5 cubic feet.	Composition in 100 volumes.					
		Hydrogen, H.	Marsh gas, CH_4.	Carbonic oxide, CO.	Heavy Hydrocarbons $(C_nH_2)_n$.	Equal to Olefiant gas, C_2H_4.	Nitrogen, Oxygen and Carbonic acid.
Cannel gas	34·4	25·82	51·20	7·85	13·06	(22·08)	2·07
Coal gas	13·0	47·60	41 53	7·82	3·05	(6·97)	..

The gas is purified by condensation and by absorption.

(1.) By *condensation* (refrigerators) the solid and liquid impurities, such as water, tar, etc., are removed.

(2.) By *absorption* (lime or oxide of iron purifiers), the carbonic acid, the presence of 1 per cent. of which is said to decrease the light 6 per cent., and the sulphur present as sulphuretted hydrogen, and to a certain extent in other forms, are removed.

Flame.

Flame results from the combination of two gases under the influence of heat. A gas to burn, therefore, is one essential condition of flame, hence, a diamond cannot burn with flame, because it cannot be volatilized. Further, it is essential that the

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temperature necessary to effect the union of the gases should be maintained. Hence, a mass of cold metal introduced into a flame will extinguish it.

The terms "*combustible*" and "*supporter of combustion*" are, however, merely conventional, inasmuch as air may be made to burn in coal gas.

The temperature at which this combination of different gases (*i. e.*, combustion) occurs, varies with different gases. Thus, *phosphoretted hydrogen* ignites at ordinary temperatures, *carbon disulphide* vapor at 419° F. (215° C.), whilst *marsh gas* needs a temperature little short of actual flame to effect its ignition.

Combustion may proceed both *without flame*, as instanced by a smouldering taper, or by the action of a hot platinum wire on mixed air and coal gas; and *with flame*, as in the ordinary cases of combustion.

An ordinary flame burning in air, is an envelope dividing the combustible gas within from the supporter of combustion without. It consists of several parts:—

(1.) A dark inner cone of unburnt gas. This is surrounded by—

(2.) A luminous cone of partially burnt gas. It is in this cone that the carbon is separated and dense hydrocarbons formed. This occurs as follows:—The air present is insufficient to burn both the hydrogen and the carbon of the hydrocarbon; consequently, the hydrogen having a greater affinity for oxygen than the carbon, combines with it, and the carbon is set free, which, becoming ignited in the burning hydrogen, renders the flame luminous. This luminous cone is surrounded by—

(3.) A non-luminous but intensely hot cone of completely-burnt gas.

(4.) At the bottom part of the flame is a portion where the combustion is complete, and where this division into the cones described, is not apparent.

In a *blow-pipe* flame a free supply of air is effected within the flame. Thus, the carbon of the hydro-carbon is burnt as well as the hydrogen. A blow-pipe flame consists of two parts, each part having a different chemical power. (α.) *The point of the inner cone* has a *reducing action*, due to the presence of an *excess of carbon* in the form of carbonic oxide, which is ready to combine with more oxygen. (β.) *The point of the outer cone* has an *oxidizing action*, due to the presence of an *excess of oxygen*.

The heat of a flame depends on the energy of the chemical combination. Thus the heat of a flame often bears no relationship whatsoever to the light. The oxy-hydrogen jet is non-luminous but enormously hot, the energy of the chemical action being intense. If lime be introduced into the jet the light becomes intense, but the heat is reduced, inasmuch as the lime not only does not contribute to the chemical action, but conducts the heat away.

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The light of a flame depends on several circumstances. (*a.*) In most cases, but not necessarily, as Frankland as shown, light depends *on solid, incandescent particles.* Thus, when solid particles are introduced into the colorless flame of hydrogen it is rendered luminous. We may, however, have a luminous flame without solid particles. A bright light is produced, for example, when metallic arsenic is burnt in oxygen, although the metal and the product of its combustion are both gaseous at the temperature of the flame. A mixture of nitrogen dioxide and carbonic disulphide again, burns with a luminous flame. (*β.*) *Temperature.* Thus sulphur, phosphorus, and other bodies give more light when burnt in oxygen than in air. The nitrogen in the latter not only contributes nothing to the energy of the combustion, but actually lowers the temperature, by removing the heat resulting from the combination of the burning body with the oxygen. (*γ.*) *Density of the gases.* (1.) *The density of the gas supporting combustion.* An alcohol flame burns with a very feeble light in air at 30° Bar. Pr., but with a good light in an atmosphere at 120° Bar. Pr. A candle gives less light on the top of the mountain than in the valley, although the tallow may be consumed at the same rate in both cases. Thus *increased* light results from *condensing*, and *decreased* light from *rarefying* the surrounding atmosphere. (2.) *The density of the combustible gas and the products of the combustion.* It would appear that luminosity is closely related to the vapor densities of the products, the higher the specific gravity of the products, the more intense the light. Thus, *e. g.*, when hydrogen is burnt in *air*, it produces water, which has a density of 9; whilst in *chlorine*, it forms hydrochloric acid, which has a density of 18·25. Hence, the light produced by burning hydrogen in chlorine, is much greater than that produced by burning hydrogen in air. Sulphur burnt in oxygen forms SO_2 (density 32); phosphorus when burnt in oxygen forms P_2O_5 (density 142); hence the greater light of the latter compared with the former.

The color of a flame depends on the kind of solid particles it contains. Thus sodium renders a flame yellow, and lithium red. Further there are cases where the temperature of the gas before combustion affects the color of the flame, as happens with carbonic oxide, the cold gas giving a blue, and the hot gas a yellowish-red flame.

We may here note that to obtain a maximum light from any flame:—

(1.) *The supply of air must not be excessive,* otherwise combustion will be too complete, the luminosity of the flame being decreased for two reasons, (*a*) that the carbon particles are consumed before they are sufficiently heated to emit light, and (*β*) that the excess of atmospheric nitrogen serves to cool the flame, thereby decreasing its illuminating power. This is illustrated by blowing on a flame, or by increasing the draught by lengthening the chimney.

(2.) *The supply of air must not be too limited,* otherwise the carbon passes off unburnt. The flame thus becomes smoky.

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COMPOUND OF HYDROGEN AND SILICON.

Silicic Hydride (H_4Si).

Synonym.—*Hydride of Silicon.*

Preparation.—(1.) By decomposing magnesic silicide with dilute hydrochloric acid. (Wöhler.)

(2.) By passing a galvanic current, the positive pole consisting of aluminium containing silicon, through a sodic chloride solution.

Properties.—A colorless gas. When impure it fires spontaneously in air, giving off white fumes of amorphous silica. The pure gas does not ignite spontaneously. It is decomposed by heat. It precipitates many metallic solutions but not those of lead or platinum.

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SECTION II.—THE METALS.

CHAPTER X.

GENERAL REMARKS ON THE METALS.

Derivation and Definition of a Metal—Order of Discovery—Natural History—Physical and Sensible Properties—Chemical Properties—The Oxides—Classification of the Metals.

Derivation.—Μέταλλον a metal. The word is found in every modern language.

Definition.—Our definition of a metal is twofold. *Physically*, "a metal is an opaque body, having a metallic lustre, and possessing for the most part a good conducting power for heat and electricity." *Chemically*, "it is an element capable of forming a base by its combination with oxygen, and a salt by its combination with a salt radical."

The division, however, of inorganic bodies into metals and metalloids is, strictly speaking, one of convenience only.

Order of Discovery.—Seven metals were known to the ancients (viz., Au, Ag, Cu, Pb, Fe, Hg, Sn); one was discovered in the fifteenth century (viz., Sb); two in the sixteenth (viz., Bi and Zn); eleven in the eighteenth (viz, As, Cr, Co, Mn, Mo, Ni, Pt, Te, Ti, W, U); and the rest in the nineteenth.

Natural History.—(α.) In the *mineral* kingdom, the metals are found either (1) native, in a free state as gold, silver, etc., or as alloys, as *e. g.*, gold with silver, gold with palladium, etc.; or (2) in combination with sulphur (galena, PbS), with oxygen (hæmatite, Fe_2O_3), or with the haloids (common salt, NaCl); or (3) as oxy-salts, as *e.g.*, sulphates (heavy spar, $BaSO_4$), carbonates (strontianite, $SrCO_3$), phosphates (apatite), etc. (β.) In the *vegetable kingdom*, sodium and potassium are found in all plants, and manganese, silver and lithium in most. (γ.) In the *animal kingdom*, iron is found in the blood, manganese in the hair, calcium in the bones, etc.

As regards *distribution*, some are widely distributed over the whole crust of the earth (*e. g.*, Ca, Al, Mg, Na, Fe), whilst others are found in small quantities only, and in few localities. Usually, they occur in cracks (lodes), in particular rocks (as *e.g.*, Au, Ag, etc.), whilst in other cases, ores, such as ironstone, are found in the more recent sedimentary formations.

I. Sensible and Physical Properties.—(1.) *Color.* This varies as follows:—(α). Red (Cu). (β.) Bright yellow (Au). (γ.) Pale yellow

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(Ba). (δ.) Reddish grey (Co, Ni, Bi). (ε.) Bluish (Pb, Zn, Cd). (ζ.) Grey (Fe, Mo, W, U, Mn, Sb), and (η.) White, which includes nearly all the remainder (lunar metals).

(2.) *Taste and smell.* The *taste* of the metals is usually astringent (metallic taste). This is probably dependent on some chemical or electrical effect set up by the action of the saliva, and is often lost when they exist in combination (as NaCl). They possess generally but little *odor*. Iron, copper, and some other metals when rubbed give out a peculiar smell, and arsenicum when heated emits a garlic odor.

(3.) *Lustre.* In their massive and polished condition, but not when finely divided, the metals generally possess a "metallic lustre," depending on the almost total reflexion of the rays of light from their surface. Certain metalloids, moreover, also possess a certain degree of lustre, as *e. g.*, iodine, silicium, graphite, etc.

(4.) *Opacity.* The metals are almost perfectly opaque to light. Fine gold leaf, however, is said to transmit a green light (Faraday, Med. Gazette, Vol. 1, 1845); silver leaf, a purple light; mercury, a blue light (Melseus and Arago, Chemical Gazette, February 1, 1846) We must be careful not to confound the passage of light through cracks, accompanied by the phenomena of diffraction, with the actual transparency of the metal.

(5.) *Texture.* (α.) Some metals have a fibrous texture (Fe); (β.) some are lamellated (Zn, Bi, Sb); (γ.) and some are crystalline (Cu, etc.)

(6.) *Crystalline form.* Most metals may be made to crystallise. The crystals may be formed by such means as the following:—

(α.) By fusion and slow cooling (Bi, Pb).

(β.) By precipitation with another metal or non-metal (Ag by Hg or P; Pb by Zn, etc.).

(γ.) By sublimation (As).

(δ.) By solution (Tin as in the moirée metallique; gold from an ethereal solution).

(ε.) By electrolysis.

The crystals generally belong to the cubic system, but they are sometimes found in rhombohedra and hexagons, as *e. g.*, zinc, arsenicum, antimony, nickel. (Chemical Gazette, 1848, p. 165.)

(7.) *Hardness.* This varies greatly. (α.) Hydrogen is believed to be a gaseous metal, whilst (β) mercury is liquid, and gallium melts by the heat of the hand. (γ.) Some are so soft that they can be indented with the nail (K, Na). (δ.) Others can be cut with a knife (Pb, Au, Ag); (ε.) whilst the majority are extremely hard (Sn, W, Fe, Ir, etc.)

The same metal may present great differences in hardness. Thus iron may be rendered sufficiently soft to be cut with a steel saw, or so hard that it will scratch glass.

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(8.) *Elasticity and sonorousness.* The sound-giving power of a body is intimately associated with its elasticity, or "power of returning to its original shape when disturbed."

(α.) Some metals are very elastic (Fe, Mn, Al, Ag); (β), others bend, but when let go do not return to their original shape (Pb, Sn, etc.), whilst (γ) others are brittle (As, Bi, etc.)

(9.) *Malleability, i. e.,* "The capability of forming thin leaves when hammered or rolled." (α.) Some metals are very malleable. The following is the order of the malleability of the malleable metals, commencing with those in which the property is most marked, viz., Au, Ag, Cu, Pt, Pd, Fe, Al, Sn, Zn, Pb, Cd, Ni, Co. The alkaline metals and frozen mercury are also malleable. (β.) The remaining metals are not malleable.

(10.) *Ductility, i. e.,* "The property of being drawn into fine wire." This property is closely but not necessarily related to malleability. Iron is a less malleable metal than copper, but more ductile. Tin is less ductile than zinc, but more malleable.

The order of the ductility of the ductile metals, beginning with those most ductile, is as follows—Au, Ag, Pt, Fe, Cu, Pd, Cd, Co, Ni, Al, Zn, Sn, Tl, Mg, Li.

Some *non-metallic bodies,* in a state of fusion, are also very ductile, such as sulphur.

(11.) *Tenacity, i. e.,* "The property of resisting weight." This is measured by the weight a given sized wire can support, the weights being added as nearly as possible within the same time. Lead being taken as 1, the following numbers represent the relative tenacity of certain metals—Pb 1; Cd 1·2; Sn 1·3; Au 5·6; Zn 8·0; Ag 8·5; Pt 13; Pd 15; Cu 17; Fe 26. This tenacity is influenced by many circumstances, as, *e.g.*—(α.) By the purity of the metal. (β.) By the *temperature.* Thus heat diminishes tenacity. Iron is more tenacious when heated to 212° F. (100° C.) than when cold, but when heated above this temperature, its tenacity is lessened. (γ). By *annealing.* Thus the tenacity of gold, by annealing, is reduced one-half; platinum, one-third; iron, one-fourth, etc.

(12.) "*Brittleness, i. e.,* "The property of breaking into small pieces when hammered." This varies greatly. The disintegration of gold or copper requires great force, whilst bismuth and antimony are, on the contrary, very brittle. Brittleness is frequently influenced by temperature. Thus, cold zinc is brittle, whilst hot zinc is malleable.

(13.) *Specific gravity.* This varies greatly from lithium, which has one-half the specific gravity of water, to platinum which has twenty-one times its density. (*See* Table of Elements.) It will be noticed that the *lightest* metals, such as K, Na and Li, are the *most* oxidizable, whilst the *heaviest,* such as Pt, Ir, etc., are the *least* oxidizable. It has been remarked that the specific gravity is increased by hammering and rolling.

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(14.) *Thermotic properties.* (α.) *All metals expand by heat and contract by cold.* Lead, however, after it has been heated, does not, on cooling, return to its original size. Each metal possesses its own rate of expansion. The expansion of the metals generally is fairly uniform for equal increments of heat up to 212° F. (100° C.), but beyond this point expansion becomes irregular.

(β.) *All metals conduct heat,* but their conductivity varies. Thus, if the conduction of silver be taken to equal 100, copper equals 74, iron 12, lead 9, platinum 8, bismuth 2, etc. In estimating the conductivity of a metal for heat, its specific heat must always be taken into account.

(γ.) *Fusibility, i. e.,* the change from a solid to a liquid state by the action of heat," (*fundo,* I pour out).—The melting points of the metals vary greatly. Thus, mercury fuses at —37·9° F. (—38·8° C.); sodium and potassium between 143° and 212° F. (60° and 100° C.); silver, copper, and gold at a bright red heat (1832° to 2012° F., or 1000° to 1100° C.); iron at a white heat (2732° to 4462° F., or 1500° to 2500° C.); whilst others, such as platinum, etc., need the heat of the oxy-hydrogen blow-pipe, or voltaic arc, to effect their fusion.

Welding implies the union of metals by pressure, when brought to the pasty state, that is, a stage previous to complete fusion (*e.g.,* Fe, Pt, Tl, Li, K, Pd).

(δ.) *Volatility, i. e.,* "the capability of being converted into vapor," (*volo,* I fly).

(1.) Some metals are volatile at ordinary temperatures (Hg).

(2.) Others are volatile below redness (K, Na, As). In the case of arsenicum, it volatizes before it melts; hence, in order to effect its fusion, the heat must be applied to the metal under pressure.

(3.) Others are volatile in an ordinary fire (Mg, Zn, Cd).

(4.) Others are volatile by the heat of the blast furnace (Cu, Pb, Ag).

(5.) Others are *almost,* but not absolutely non-volatile (as Au, Pt).

(ε.) *Specific heat* (*see* page 37). If it be desired to raise the temperature of 1 kilo. of platinum and 1 kilo. of water respectively 1 degree, we should find that it would require 31 times as much heat to raise the water as it would to raise the platinum. This quantity is called the *specific heat* of a metal. Therefore if the specific heat of water = 1, the specific heat of platinum = $\frac{1}{31}$ or 0·032.

If *equal weights* of the metals be taken, the specific heat will be found to *vary* with the metal; but if *atomic weights* of the metals be taken, the specific heat (or *atomic heat* as it is called in this case) will be found in all cases to be *equal.*

Atomic heat therefore is specific heat estimated not on *equal weights* as 1 kilo, but on *atomic weights.* It may also be estimated by multiplying the specific heat by the atomic weight.

It will further be observed that the atomic weight of a metal in any

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doubtful case, may be checked by determining its specific heat. This relationship is not, however, peculiar to the metals.

(15.) *Electrical Properties.* (α.) *Conductivity.* All metals conduct electricity, but their electric conductivity is unequal. Thus, the conducting power of silver and copper is five times greater than that of iron and platinum, and twelve times greater than that of lead. Hydrogen is not an electrical conductor, but it is to be noted that the metals generally are not conductors in a state of vapor.

(β.) *The metals, when liberated from their compounds, appear at the negative pole of the battery.*

(16.) *Magnetic Properties.* (α.) Certain metals are magnetic at ordinary temperatures, their magnetic power being generally increased by cold (Fe, Ni, Co). (β.) Other metals are attracted equally by either pole of a magnet. If such metals be suspended in the form of a bar over the poles of a horseshoe magnet, they arrange themselves *axially;* that is, with their ends over each pole (Fe, Ni, Co, Mn, Cr, Pd, Pt, Os). These metals are called magnetics. (γ.) Other metals are *repelled* by a magnet; when bars of such metals are suspended over the poles of a horseshoe magnet they arrange themselves *equatorially;* that is, contrary to the poles (Bi, Sb, As, Zn, Pb, Sn, Hg, Au). These metals are called diamagnetics.

(17.) *Power of absorbing gases* (occlusion). Thus, platinum and iron at a red heat freely absorb hydrogen (Deville and Troost). Platinum is capable of absorbing 3·8 volumes of hydrogen at a red heat, whilst palladium absorbs at a heat below 100° C. 643 times its volume.

This power of hydrogen (hydrogenium) of forming an alloy, and its near relationship in this state to the metals (as, *e.g.*, its power of conducting heat and electricity, its magnetic properties, etc.) have led chemists to regard hydrogen gas as the vapor of a highly volatile metal.

II. Chemical Properties.—(1.) The metals being elements, resist decomposition. We shall consider first of all their combinations with oxygen.

THE OXIDES.

All the metals may be oxidized, and often in several proportions. The oxides are closely analogous to the chlorides; oxides being regarded as substitution derivatives of one or more molecules of H_2O, and chlorides as derivatives of one or more molecules of HCl. There are, however, certain oxides, as PbO_2, without chlorine analogues. The oxides generally are opaque, earthy-looking bodies, and destitute of metallic lustre.

A *hydroxide* is a compound where only a part of the hydrogen of one or more molecules of water is replaced by a metal. Thus, K′ being a monad and Ca″ a dyad, and Al^{vi} a hexad—

KHO=potassic hydroxide; $Ca''(HO)_2$=calcic hydroxide;

$Al_2^{VI}(HO)_6$=aluminic hydroxide.

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The soluble hydroxides have a strong alkaline reaction.

All metals except gold, platinum, iridium, rhodium, and ruthenium are capable of combining with oxygen directly; that is, without the intervention of a third element. Their rapidity of oxidation is largely influenced (α) By the presence of *moisture*, pure dry oxygen having very little action on the metals at ordinary temperatures, except on the alkaline metals; (β.) By the *temperature;* and (γ.) By the condition of the metals themselves; that is, whether they are in a finely divided or in a massive state.

It is to be noted that *the lightest metals* are those *most easily oxidized* (as Na, K, etc.), and the *heaviest metals* those *least easily oxidized* (as Au, Pt). Thus the attraction of a metal for oxygen is inversely to its specific gravity. We may classify the action of oxygen on the metals as follows:—

(A.) *Metals that combine with oxygen readily and part from it with difficulty.* Of these there are several classes.

(1.) Metals that combine with the oxygen of air and water *at ordinary temperatures,* liberating hydrogen in the case of the water (K, Na, Li, Ba, Sr, Ca).

(2.) Metals that combine with atmospheric oxygen slowly, and with the oxygen of water only when heated (Mg, Zn, Al, Cd, Mn, Ni, Co, Fe).

(These metals decompose HCl and H_2SO_4 at common temperatures, liberating hydrogen).

(3.) Metals that combine with atmospheric oxygen very slowly, and with the oxygen of water only when the metal is red-hot (Sb, As, Sn).

(These metals will not decompose HCl and H_2SO_4 at common temperatures, but will decompose KHO, liberating hydrogen.)

(4.) Metals that combine with atmospheric oxygen slowly at ordinary temperatures and rapidly when red-hot, but will not decompose water at any temperature (Cu, Pb, Bi). These oxides cannot be decomposed *by heat alone.*

(B.) *Metals that combine with oxygen with difficulty and part from it readily* (noble metals).

Thus, in the case of mercury both oxidation and deoxidation may be easily effected by heat.

Preparation of Oxides.—I. *Hydrated metallic oxides.* By precipitating a metallic salt with an alkaline hydrate:—

$$ZnSO_4 + 2KHO = K_2SO_4 + ZnH_2O_2.$$

Zincic sulphate + Potassic hydrate = Potassic sulphate + Hydrated Zincic oxide.

$$[SO_2Zno'' + 2OKH = SO_2Ko_2 + ZnHo_2.$$

II. *Anhydrous oxides.* (1.) By burning a metal in air or oxygen, as in the case of Zn, As, Pb, K, Na. (A *protoxide* may often be converted into a *peroxide* by heating it in a current of air or oxygen.

(2.) By the ignition of—

(α.) *Nitrates,* nitric anhydride being expelled (Hg, Bi, Cu, Ba, Sr).

(β.) *Carbonates,* CO_2 being expelled. (This occurs with all carbonates excepting those of Cs, Rb, Na, K, Ba, Li).

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(γ.) *Hydrated oxides* (Fe).

(δ.) *Sulphates* (as those of alumina, ferric oxide).

(3.) All acid oxides may be prepared by deflagrating the metal or its sulphide with nitre.

Varieties of Oxides.—Oxides may be divided into three classes:

I. *Basic or alkaline oxides; i.e.*, oxides that act as bases (Ag_2O, PbO).

II. *Neutral, saline or indifferent oxides; i.e.*, oxides that have very very slight disposition to enter into combination (MnO_2).

III. *Acid oxides or metallic anhydrides; i.e.*, oxides which when hydrated, form acids (As_2O_5).

Table of Oxides.

Names.	Formula.	Types.	Metals belonging to the group.	Characteristics of group.
I. Suboxides ..	$'M'_2O$	$'Cu'_2O$	Cu, Pb, Hg	*Basic.* A dyad metal, becomes equivalent to a single H atom. Unstable bodies easily decomposed.
II. Monoxides ..	(α.) M'_2O (β.) $M''O$	Ag_2O $Ca''O$	The metals of the alkalies with Tl', Ag', and the metals of the alkaline earths: with Mg'', Zn'', Cd'', La'', Di'', Th''.	*Basic.* The alkaline oxides combine with water to form hydrates, one molecule of each forming *two* molecules of hydrate ($Na_2O+H_2O=2NaHO$).
			Protoxides of Ce'', U'', Co'', Ni'', Fe'', Cr'', Mn'', Sn'', Cu'', Pb'', Hg'', Pd''	The alkaline earth-oxides also form hydrates, one molecule each of the oxide and water forming *one* molecule of hydrate ($CaO+H_2O=CaH_2O_2$).
III. Sesquioxides	M'''_2O_3 $'M'''_2O_3$	$Al_2'''O_3$	Al, Ce, Fe, Mn, Cr, Sb, Bi, U.	Feebly *Basic.* Salts redden litmus.
			Co, Ni.	*Neutral.* Evolve Cl with HCl.
			As, Au,	Feebly *acid.*
IV. Three-fourths Oxides....	M_3O_4 or $M''O+M'''_2O_3$	Fe_3O_4	Fe, Cr, U, Mn, Ni, Co,	*Neutral.* By the action of acids they form $MO+M_2O_3$.
			Also double oxides as FeO,Cr_2O_3 (chrome iron-stone); MgO,Al_2O_3 (spinelle); $ZnOAl_2O_3$ (Gahnite)	
V. Dioxides	(α.) $M^{iv}O_2$	PtO_2	Pt, Pd	Feebly *Basic.* Form hydrates ($PtO_2,2H_2O$.)
	(β.) M'_2O_2	Na_2O_2	Na, Ag, Ba, Ca, Sr, Mn, Pb	Either *neutral*, or else form very unstable salts which evolve O with H_2SO_4. With HCl they either furnish hydroxyl or evolve chlorine.
	(γ.) $M^{iv}O_2$	SnO_2	Sn, Ti	*Acid* as hydrates.
VI. Trioxides ..	$M^{vi}O_3$	CrO_3	Cr, Mo, W, Ru, Fe, Mn	*Acid* (metallic anhydrides.)
VII. Anhydrides..	M_2O_5	As_2O_5	As, V, Sb,	*Acid.*

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Properties of the Oxides.—(*a.*) *Physical*, etc. The oxides are solid bodies, of various colors, having generally a more or less metallic taste, but no smell. They are harder than the metals from which they are formed, but of less specific gravity.

Action of heat on metallic oxides.—(A.) *Fusibility.* An oxide of a metal is generally less fusible than the metal. To this general rule there are three exceptions, viz., FeO, Cr_2O_3, MoO_3.

(i.) Some oxides are volatile at ordinary temperatures (As_2O_3, Sb_2O_3, OsO_4).

(ii.) Some oxides fuse at a red heat (K_2O, Na_2O, PbO, Bi_2O_3,).

(iii.) Some oxides require a white heat (CuO, MoO_3, Cr_2O_3, Fe_3O_4).

(iv.) Some oxides need the heat of the oxy-hydrogen jet (BaO, SrO, Al_2O_3).

(v.) Some oxides are absolutely infusible (zirconia, yttria).

(B.) *Reduction.* At a red heat certain oxides are completely, whilst others are partially, decomposed.

(i.) *Reduction is complete* in the case of the oxides of Au, Ag, Pt, Pd, Hg, etc.

(ii.) *Reduction is partial* in the case of such peroxides as PbO_2, Co_2O_3, Ni_2O_3, BaO_2, which by heat become protoxides, as Pb″O, Co″O, Ni″O, Ba″O. Again, the anhydrides As_2O_5, and CrO_3 become when heated As_2O_3 and Cr_2O_3, and MnO_2 becomes Mn_3O_4.

(C.) *Heated in a current of hydrogen*, all the oxides may be completely reduced, excepting Al_2O_3, Cr_2O_3, MnO, and the oxides of the alkalies and of the alkaline earths. The oxides of mercury, silver, platinum and gold, are reduced at 212° F. (100° C), and the rest at a red heat. Example—($CuO + H_2 = Cu + H_2O$).

[Note here *reciprocal action.* Free hydrogen reduces the oxide of iron, forming steam; steam passed over red hot iron yields oxide of iron and free hydrogen.]

(D.) *Heated with carbon*, all the oxides may be reduced, except the oxides of lithium and the oxides of the earth-metals. In the case of the readily oxidizable metals (as K, Zn, Fe), CO is evolved, the CO_2 first produced being afterwards decomposed; but with the less readily oxidizable metals (such as Cu, Pb, etc.) the CO_2 is evolved without suffering further decomposition.

Action of electricity on metallic oxides. The protoxides are insulators, whilst some of the peroxides are conductors.

Action of Water on the Oxides.—The oxides of the alkaline metals, together with the oxides of barium, strontium, calcium, and thallium, and the hydrated acid oxides, are freely soluble in water; the oxides of lead, silver, and mercury, are slightly soluble, and the remainder are insoluble.

Most oxides unite chemically with water to form hydroxides, or hydrated oxides. All hydroxides neutralise acids. In some cases the

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metal will not part with its water molecule at any temperature, as in the case of the alkaline hydrates, whilst in the case of other hydrates heat will easily effect the separation.

(β.) *Chemical.*—The chemical properties of the oxides are very varied, depending to a great extent on the different degrees of oxidation of which the metal is capable.

Thus of the oxides of manganese, MnO and Mn_2O_3 are basic oxides; Mn_3O_4 is an indifferent oxide (that is neither basic nor acid), whilst MnO_3 and Mn_2O_7 are acid oxides. As a rule the higher the oxide the less basic it becomes.

Action of Chlorine on the oxides.—All metallic oxides are decomposed when heated in an atmosphere of chlorine except magnesia and the oxides of the earths. The metal is reduced in the case of the oxides of the noble metals, whilst in other cases a metallic chloride is formed. Chlorine decomposes certain oxides, as Ag_2O, at ordinary temperatures.

With the hydrated oxides suspended in water, chlorine forms in the case of the alkalies and alkaline earths bleaching compounds (see page 280), whilst with the hydrated oxides of iron, manganese, chromium, cobalt, and nickel, it forms either a mixture of a chloride and a hydrated sesquioxide ($3CoH_2O_2 + Cl_2 = CoCl_2 + Co_2H_6O_6$); or if the liquid be strongly alkaline, a metallic sesquioxide only ($2CoH_2O_2 + 2KHO + Cl_2 = Co_2H_6O_6 + 2KCl$); or if the metal be capable of forming an acid, a salt results by the action of the acid on an excess of the alkali ($Fe_2H_6O_6 + 10KHO + 3Cl_2 = 2K_2FeO_4 + 6KCl + 8H_2O$).

Action of sulphur on the oxides.—At high temperatures sulphur decomposes most metallic oxides, with the exception of MgO, Al_2O_3, Cr_2O_3, SnO_2, TiO_2, and the oxides of the earths proper. In most cases a sulphide is formed, and SO_2 escapes; whilst in the case of the oxides of the alkalies and alkaline earths, a mixture of a *sulphide* and a *sulphate* of the metal is formed.

Action of nascent hydrogen on the oxides.—Most oxides are decomposed by nascent hydrogen.

Action of acids on the metallic oxides.—(1.) *Hydrochloric acid.*—In most cases, water and a corresponding metallic chloride are formed. Thus—

Cuprous oxide forms *cuprous chloride* ($Cu_2O + 2HCl = H_2O + Cu_2Cl_2$).
Sesquioxides form *sesquichlorides* ($Fe_2O_3 + 6HCl = 3H_2O + Fe_2Cl_6$).
Binoxides form *tetrachlorides* ($SnO_2 + 4HCl = 2H_2O + SnCl_4$).

If chlorides corresponding to the oxides do not exist, other changes result; thus, in the case of the following oxides, the following reactions occur:—

Antimonic oxide; $Sb_2O_5 + 6HCl = 3H_2O + 2SbCl_3$.
Dimanganic trioxide; $Mn_2O_3 + 6HCl = 3H_2O + 2MnCl_2 + Cl_2$.
Manganic peroxide; $MnO_2 + 4HCl = 2H_2O + MnCl_2 + Cl_2$.
Chromic anhydride; $2CrO_3 + 12HCl = 6H_2O + Cr_2Cl_6 + 3Cl_2$.

(2.) *Sulphuric acid.*—Sulphuric acid combines with *basic oxides* to

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form salts, the oil of vitriol displacing all other acids with which the oxide may be united; whilst on either *indifferent* or on *acid oxides* the sulphuric acid causes an escape of oxygen, and combines with the base formed. Thus—$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$.

In all cases when sulphuric acid acts on *oxides*, water is formed, whilst when it acts on *metals*, hydrogen is liberated.

(3.) *Hydro-sulphuric acid* (H_2S). — Most metallic oxides (except magnesia, alumina, and chromic oxide) are converted by H_2S into sulphides or sulph-hydrates of the metal and water—

$$PbO + H_2S = PbS + H_2O.$$

We may now return to the metals themselves, and consider their other chemical relations.

(2.) *Action of the haloid elements.*—*Chlorine* combines *directly* with all the metals, often at common temperatures (as *e.g.*, with Sb), but under all circumstances by the application of heat (*see* page 75). Bromine, iodine, and fluorine also combine with most metals directly.

(3.) *Action of carbon.*—Iron, manganese, palladium, iridium, and a few other metals, form compounds with carbon, called *carbides*. The carbides are generally more fusible than the metals themselves.

(4.) *Action of phosphorus.*—Phosphorus combines with the metals to form *phosphides*.

(5.) *Action of nitrogen.*—The affinity of nitrogen for the metals is slight, the compounds formed, called *nitrides*, being usually explosive and difficult of examination. They are generally prepared by the action of ammonia on various oxides (Au, Ag, Pt, Cu, Hg, Fe), but in the case of vanadium, titanium, and molybdenum, direct union of the metal and nitrogen may be effected.

(6.) *Action of hydrogen.*—Hydrogen forms *hydrides* with five metals (As, Sb, Cu, Fe, K). The hydrides of arsenicum and antimony are gaseous, and are completely decomposed by a red heat. A solid hydride of arsenicum is believed to exist.

(7.) *Silicon, boron, selenium,* and *tellurium* also combine with certain of the metals to form silicides, borides, selenides and tellurides.

(8.) *Action of water on the metals* :—

(α.) Certain metals decompose water at *common temperatures* (K, Na, Li, Ba, Sr, Ca).

(β.) Others, when *the water is boiling* (Mg, Al, Cd, Mn).

(γ.) Others, when the metal is *red* hot (Sb, As, Sn, Zn, Fe, Cr, Co, Ni).

(δ.) Others, when the metal is *white* hot (Al, Pb, Bi, Cu), whilst

(ε.) Others do not decompose water at all (the noble metals).

The action of the metals on water is modified (1) by *the presence of air*, whereby the action of a metal on water is rendered more energetic; and (2) by *the contact of two metals*, whereby a galvanic current is set up, and the energy of solution intensified.

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(9.) *Action of the acids on metals.*—(A.) *Sulphuric acid* :—

(α.) Sulphuric anhydride cannot be made to combine directly with the metals.

(β.) The *concentrated* acid acts on very few metals *without heat*, whilst,

(γ.) The *dilute* acid acts on most metals at ordinary temperatures, a metallic sulphate being formed with the liberation of hydrogen (Zn, Fe, Co, Ni, Mn).

(δ.) In certain cases heat is required to bring about combination with the dilute acid, when a metallic sulphate is commonly formed and sulphurous acid liberated (Ag, Cu, Hg, As, Sb, Bi, Sn, Pb) ($Ag_2 + 2(H_2SO_4) = Ag_2SO_4 + 2H_2O + SO_2$).

(ε.) The acid (strong or dilute) has no action on gold, platinum, rhodium, or iridium. Thus, sulphuric acid is used to part silver from gold, and gold from copper.

(ζ.) When the vapor of sulphuric acid is passed over red hot platinum, it is decomposed into oxygen and sulphurous acid (see p. 57).

(B.) *Nitric acid.* Nitric acid dissolves most metals, and more readily when dilute than when concentrated. (α.) Upon *gold and platinum* nitric acid has no action; whilst (b.) *tin and antimony* are not dissolved but oxidised by nitric acid, the insoluble anhydrides SnO_2 and Sb_2O_5 being formed.

We may here note that dilute sulphuric acid by its action on metals usually liberates hydrogen, but that nitric acid does not. No doubt, however, hydrogen is in the first instance set free, but owing to the intense action of the nitric acid the hydrogen formed is rapidly oxidised.

Many products result from the action of nitric acid on the metals, of which we may note the following :—

(α.) *Nitrous oxide* (N_2O). By the action of the dilute acid on an energetic metal, such as zinc :—

$$4Zn + 10HNO_3 = 4(Zn2NO_3) + 5H_2O + N_2O.$$

Zinc + Nitric acid = Zincic nitrate + Water + Nitrous oxide.

$$4Zn + 10\mathbf{N}O_2Ho = 4\left\{\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}\right.Zno'' + 5\mathbf{O}H_2 + \mathbf{O}N_2.$$

(β.) *Nitric oxide* (N_2O_2). By the action of an acid of specific gravity 1·25 on such metals as Cu and Hg :—

$$3Cu + 8HNO_3 = 3(Cu2NO_3) + 4H_2O + N_2O_2.$$

Copper + Nitric acid = Cupric nitrate + Water + Nitric oxide.

$$3Cu + 8\mathbf{N}O_2Ho = 3\left\{\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}\right.Cuo'' + 4\mathbf{O}H_2 + \left\{\begin{matrix}\mathbf{N}O.\\ \mathbf{N}O.\end{matrix}\right.$$

(γ.) *Nitrous anhydride* (N_2O_3). By the action of the acid on silver or palladium :—

$$2Ag_2 + 6HNO_3 = 4AgNO_3 + 3H_2O + N_2O_3.$$

Silver + Nitric acid = Argentic nitrate + Water + Nitrous anhydride.

$$2Ag_2 + 6\mathbf{N}O_2Ho = 4\mathbf{N}O_2Ago + 3\mathbf{O}H_2 + \left\{\begin{matrix}\mathbf{N}O.\\ O.\\ \mathbf{N}O.\end{matrix}\right.$$

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(δ.) *Nitric peroxide* (N_2O_4), By the action of an acid of specific gravity 1·42 on tin, copper, etc. :—

$$5Sn + 20HNO_3 = Sn_5O_{10}, 5H_2O + 5H_2O + 10N_2O_4.$$
Tin + Nitric acid = Metastannic acid + Water + Nitric Peroxide.
$$5Sn + 20\mathbf{N}O_2Ho = Sn_5O_5Ho_{10} + 5\mathbf{O}H_2 + 10\mathbf{N}_2O_4.$$

(ε.) *Nitrogen.* By the action of the acid on copper at a high temperature :—

$$5Cu + 12HNO_3 = 5(Cu2NO_3) + 6H_2O + N_2.$$

(ζ.) *Ammonia* (NH_3). Any metal capable of decomposing water will generate ammonia in dilute nitric acid. (α) In the first stage nascent hydrogen is set free; (β) this reacts on the nitric acid, forming water with the oxygen, and ammonia with the nitrogen; (γ) and lastly, the excess of ammonia combines with the excess of acid. Thus :—

(α.) $2HNO_3 + Zn = Zn2NO_3 + H_2.$
Nitric acid + Zinc = Zincic nitrate + Hydrogen.
$2\mathbf{N}O_2Ho + Zn = \mathbf{N}_2O_4Zno'' + H_2.$

(β.) $2HNO_3 + 9H_2 = 2NH_3 + 6H_2O.$
Nitric acid + Hydrogen = Ammonia + Water.
$2\mathbf{N}O_2Ho + 9H_2 = 2\mathbf{N}H_3 + 6\mathbf{O}H_2.$

(γ.) $2HNO_3 + 2NH_3 = 2(NH_4O, NO_2).$
Nitric acid + Ammonia = Ammonic nitrate.
$2\mathbf{N}O_2Ho + 2\mathbf{N}H_3 = 2\mathbf{N}O_2(NH_4O).$

(C.) *Hydrochloric acid.* The affinity of a metal for chlorine is somewhat greater than its affinity for oxygen; hence the action of hydrochloric acid on a metal is always a little in excess of the action of water on a metal. All metals that decompose water at a red heat, decompose hydrochloric acid, hydrogen being liberated and a chloride of the metal formed ($2HCl + Zn = ZnCl_2 + H_2$). It is to be noted that—

(α.) *Silver* does not decompose water at any temperature, but is *slowly* decomposed and dissolved by strong hydrochloric acid.

(β.) *Gold and platinum* are not acted on by hydrochloric acid unless free chlorine be present.

(D.) *Nitro-muriatic acid* (aqua regia). This is a mixture of one part of HNO_3 and three parts of HCl. Gold, platinum and the noble metals generally are dissolved by it, free chlorine, together with red fumes (*viz.*, the oxy-chlorides of nitrogen NOCl and $NOCl_2$) being evolved.

(E.) *Hydrosulphuric acid* (sulphuretted hydrogen).

(α.) On certain metals sulphuretted hydrogen acts *at ordinary temperatures* (Hg, Ag); whilst

(β.) On other metals the action does not occur without heat, when the displacement of the hydrogen from the H_2S may be, either

(1.) *Complete*, as *e.g.*, $H_2S + Sn = SnS + H_2$, or

(2.) *Partial*, as *e.g.*, $2H_2S + 2K = 2KHS + H_2$.

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(10.) *Action of alkalies.* Certain metals snch as iron and copper when red hot decompose ammonia gas. When potassium is gently heated in dry ammonia, KH_2N is formed, which is regarded by some as a substitution derivative of H_3N, and by others as a compound of potassium and amidogen (H_2N).

Platinum as well as other metals are oxidised when heated with potassic hydrate.

Classification of the Metals.—The classification of the metals according to their *atomicity* has manifest advantages. The table (page 42) illustrates their arrangement accordingly.

We prefer, however, (regarding the primary object of classification as convenience,) to adopt simply a division into the various groups occurring in the ordinary process of systematic analysis, commencing with Group VI. (*the alkaline metals*) and working backwards.

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CHAPTER XI.

ALLOYS AND SALTS.

Alloys—Changes in property effected by Alloying—Acids—Bases—Salts. *Haloid Salts*—Chlorides, Bromides, Iodides, Fluorides, Sulphides, Selenides, Phosphides, Carbides, Borides, Silicides. *Oxy - Salts*—Sulphates, Selenates, Chromates, Manganates, Tungstates, Molybdates, Tellurates, Hyposulphates, Thiosulphates, Sulphites, Hyposulphates, Nitrates, Nitrites, Hyponitrites, Chlorates, Bromates, Iodates, Perchlorates, Periodates, Chlorites, Hypochlorites, Phosphates, Hypophosphites, Phosphites, Arsenates, Antimonates, Arsenites, Carbonates, Silicates, Borates. *Double Salts.*

We proceed to consider:—

I. The compounds of the metals with metals (alloys).

II. The compounds of the metals with the metalloids (salts).

ALLOYS (*ad* to, and *ligo* I bind).

Definition.—An alloy is a compound formed by the union of metals amongst themselves. If the alloy contains mercury it is then called an *amalgam.*

Are the alloys mere mechanical mixtures, or are they chemical compounds? To answer this question we must ask, Is there any evidence of *definite change* resulting from the admixture of metals, such as happens in the admixture of metalloids? Matthiessen (who has specially studied the subject of alloys) considers that alloys may be divided into two classes:—

(1.) *Physical Alloys,* or mere mechanical mixtures of metals, in which, at the time of mixture, no heat is evolved, and where each metal imparts to the alloy its properties in the proportion in which it exists in the alloy. As illustrations of this class we may mention a mixture of lead and tin, or of zinc and cadmium.

(2.) *Chemical Alloys, i.e.,* where, at the time of mixture, heat is evolved, and where the metals forming the alloy do not impart their properties to the alloy in the proportion in which they exist in it. This class includes alloys of all the metals, excepting mixtures of lead, tin, zinc, and cadmium amongst themselves.

Definite compounds no doubt exist; necessarily, however, as intensity of combination largely depends on dissimilarity of property, the ties of union are weak, and the separation of the components easy. Thus (1) heat will drive off zinc from its alloy with copper, or arsenicum from its alloy with platinum; whilst (2) slight mechanical causes, such as the mere squeezing through leather, will remove the excess of mercury from a mixture of mercury and silver.

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Change of property is the essential result of a chemical act. We shall consider now the changes that result in the formation of alloys.

I.—Changes in the Sensible and Physical Properties of Alloys.

(α.) *Color.* Thus the addition of 18 per cent. of nickel to brass renders it white (Packfong, or German silver). Similarly, an alloy of arsenicum with copper, or of platinum or palladium with gold, renders the copper and the gold white. The alloy of gold and silver has a pale greenish tint.

(β.) *Hardness.* The hardness of an alloy is usually greater than the mean hardness of the constituent metals. Thus a little copper (8·33 per cent.) is added to the gold used for coinage, in order to increase the hardness of the gold. The alloy of tin, lead, and antimony forms the hard *type-metal.* The alloy of copper and zinc forms a hard compound that may be cast or turned. The alloy of copper and tin forms a very hard bronze. Manganese or tungsten increase the hardness of steel to so great an extent, that the alloy may be used for boring through steel.

(γ.) *Elasticity and Sonorousness.* An alloy of copper and tin ($=Cu_6Sn$), or of copper with zinc or lead constitutes the sonorous *bell-metal.*

(δ.) *Malleability.* The malleability of a metal is usually decreased by alloying. Thus, if 0·5 gr. of lead be added to 1 oz. of gold, it destroys its malleability. If melted gold be kept for some time, even in the vicinity of melted tin, it becomes brittle. The alloy of two malleable metals may form a brittle alloy (*e.g.*, gold and lead); but no case is known where the alloy of two brittle metals forms other than a brittle alloy. A mixture of copper, zinc, and platinum forms a very malleable alloy; but if a trace of iron be added, in the proportion of 0·5 gr. to 4 oz. of the alloy, it renders it brittle.

(ε.) *Tenacity.* This is both increased and diminished by alloying.

(1.) *Increased.* If a gold wire be taken that will bear a strain of 25 lbs., it will be found that a similar sized one of copper will bear a strain of 25-30 lbs. If now a wire of the same gauge, made of an alloy of gold with 8·4 per cent. of copper be tested, it will be found to bear a strain of from 70-75 lbs.

(2.) *Diminished.* If a copper wire be taken which bears a strain of from 25 to 30 lbs., the same sized tin wire will be found to bear a strain of less than 7 lbs., whilst a wire formed by the alloy of equal parts of tin and copper will not bear a strain above 7 lbs.

(ζ.) *Specific Gravity.* The gravity of an alloy may be either *above* or *below* the mean of the gravities of its constituents. Standard gold consists of 11 parts of gold and 1 of copper, the specific gravity of the alloy being 17·157, the mean specific gravity being 18·47.

(η.) *Thermotic properties.* The fusing-point of an alloy is invariably

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below the mean fusing points of its constituents, just as the fusibility of double chlorides, carbonates, or silicates, is generally lower than the separate salts of which these double salts are composed. Thus an alloy of four parts of bismuth (which fuses at 507° F., or 264° C.), 2 of lead (which fuses at 607° F., or 309·5° C.), and one of tin (which fuses at 442° F., or 227·8° C.), a mixture nearly corresponding to the formula Bi_2PbSn melts below 212° F. (100° C). Platinum, which is very difficult of fusion, melts easily when alloyed with arsenicum. In the extraction of silver from lead by Pattinson's process (see Index), it is found that the part which cools last contains nearly all the silver, owing to the greater fusibility of the alloy of lead and silver.

(θ.) *The conductivity of metals for heat and electricity* is usually decreased by alloying.

II. Changes in the Chemical Properties.

These, it must be acknowledged, are not well marked.

(1.) *A certain change in the capability of a metal for oxidation may be noted as the result of alloying.* An alloy, *e.g.* of two oxidizable metals (such as an alloy of lead and tin) is generally more readily oxidized than either of its constituents.

(2.) *A change in the action of acids may be remarked.* For example —German silver is completely soluble in dilute sulphuric acid, although the acid will not attack copper, which is one of its chief constituents. An alloy of 1 part of platinum and 12 parts of silver is soluble in nitric acid, in which free platinum is insoluble. Further, the presence of iridium and rhodium, as commonly occurs in commercial platinum, renders the platinum less easily attacked by chemical reagents.

SALTS.

Acids, Bases, Salts.

Chemical nomenclature, prior to 1786, was both unsystematic and imperfect. *Acetic acid* to the older chemists was a mineral acid, because it was sour. A *salt* was regarded as a solid, crystallizable substance, soluble in water.

In 1786 Lavoisier defined an acid as "*an oxidized body, sour, capable of reddening vegetable blues, and of combining with and neutralising alkalies.*" All the acids known to Lavoisier contained oxygen; he regarded this element, therefore, as the acidifying principle of an acid, and essential to its existence (acid-begetter). A salt Lavoisier defines as "*the union of an acid,*" that is an anhydride, as we call it, but which Lavoisier and his school regarded as an acid, "*with an oxide of a metal*" (a base). Thus KO,SO_3, formed the salt sulphate of potash. This constituted "*the dualistic theory of salts.*"

In 1795 Sir H. Davy pointed out that the very type of salts (viz.

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common salt) contained neither acid nor base, and that there were bodies in existence corresponding to Lavoisier's definition of an acid, except that they contained no oxygen. Hence Lavoisier's definition of acids and salts had to be modified. Acids were consequently divided into two classes, and salts into two classes; viz.:—

(1.) *Oxyacids;* bodies containing oxygen, which, combined with an oxide of a metal (a base), formed *oxy-salts.*

(2.) *Hydracids;* bodies in which hydrogen was an essential ingredient, the combination of the radical or characteristic element of which with metals, formed *haloid salts.*

In 1812, that is, very shortly after the discovery of chlorine, Davy recognized the similarity in the action of oxyacids and of hydracids on metals. He further pointed out that all acids contained hydrogen, and that an anhydride was not an acid. He suggested that all acids were salts, and that all salts were compounds of a radical (simple or compound) with a metal. He thus laid the foundation of "*The Binary Theory of Salts.*" Lavoisier's "*Dualistic Theory*" expressed *nitrate of potash* as KO,NO_5, or a compound of the *acid* (as he regarded it) NO_5 and the *base* KO; whilst Davy's "*Binary Theory*" expressed it as KNO_6, or a compound of the *metal* potassium (K) with the *acid radical* NO_6. Moreover, Davy remarked a close similarity of constitution between oxy-salts and haloid salts, as, for example, between KCl and KNO_6.

In 1819, Berzelius introduced his Electro-Chemical Theory, according to which he regarded salts as compounds of an *electro-negative* (that is, a body attracted by the *positive* pole of a battery), and an *electro-positive* (that, is, a body attracted by the *negative* pole). All the metalloids (excepting hydrogen) were electro-negative; all the metals (including hydrogen) were electro-positive. This much remains a fact, viz., that the elements differing most in their chemical relationships usually exhibit the greatest activity of combination; but, that the chemical functions are determined *exclusively* by the electrical relationships, has been disproved by the discoveries of 1834 and following years. For *the laws of substitution* (introduced and elaborated by Dumas, Gay Lussac, Laurent, Gerhardt, etc.) prove the possibility of an electro-negative body like chlorine taking the place of an electro-positive body like hydrogen in a compound. The "theory of types" was then called in, to aid the "theory of substitution," thus paving the way for the fuller acceptance of Davy's "Binary theory."

We shall here discuss the definitions of (I.) *an acid,* (II.) *a base,* (III.) *a salt.*

I. Acids (ακη, a point).

An Acid is "*a compound containing one or more atoms of hydrogen, capable of displacement by a metal presented to it in the form of a hydrate.*"

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Acids are of different basicities, according to the number of atoms of displaceable hydrogen they contain.

A *monobasic acid* contains one atom of *displaceable hydrogen*, that is, of hydrogen that may be displaced by a metal, *e.g.* :—

HNO_3 (nitric acid) forms KNO_3, $NaNO_3$, $Ca''2(NO_3)$.

HCl (hydrochloric acid) forms KCl, NaCl, $Ca''Cl_2$.

A *polybasic acid* contains two or more atoms of displaceable hydrogen. It is called *dibasic* when it contains two atoms of displaceable hydrogen (*e.g.*, H_2SO_4); *tribasic* when it contains three atoms (*e.g.*, H_3PO_4); and so on.

Types of different Acids.

(1.) (α.) *A monobasic acid* has been regarded as formed on the type of *a single molecule of water* $\left(\begin{matrix}H\\H\end{matrix}\right\}O\Big)$ where *one* hydrogen atom of the water molecule has been displaced by a compound monatomic radical.

(β.) *The anhydride of such monobasic acid* is regarded as formed by the displacement of *both* hydrogens of the water molecule by two molecules of the compound radical.

(γ.) *The salt of a monobasic acid* is regarded as formed by the displacement of the *second* hydrogen atom of the acid, by a metal.

This will be seen as follows :—

$$(\alpha.)\ \left.\begin{matrix}NO_2\\H\end{matrix}\right\}O = HNO_3\ (acid).$$

$$(\beta.)\ \left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O = N_2O_5\ (anhydride).$$

$$(\gamma.)\ \left.\begin{matrix}NO_2\\K\end{matrix}\right\}O = KNO_3\ (salt).$$

(2.) (α.) *A dibasic acid* has been regarded as formed on the type of *a double molecule of water* $\left(\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2\Big)$, where two hydrogen atoms of the double water molecule have been displaced by a compound diatomic radical.

(β.) *The anhydride of such dibasic acid* is formed by the displacement of the four hydrogen atoms, by two atoms of the compound diatomic radical.

(γ.) *The salt of a dibasic acid* is formed by the displacement of one or both hydrogen atoms of the acid by a metal.

If one of the hydrogens only be displaced by a metal, *an acid salt* is formed; if both hydrogens be displaced by the same metal then a *normal salt* is formed; whilst if the hydrogens be displaced by different metals then a *double salt* is formed. Thus—

$$(\alpha)\ \left.\begin{matrix}SO_2\\H\end{matrix}\right\}O_2 = H_2SO_4\ (acid).$$

$$(\beta.)\ \left.\begin{matrix}SO_2\\SO_2\end{matrix}\right\}O_2 = 2SO_3\ (anhydride).$$

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$$(\gamma.)\ \left.\begin{matrix}SO_2\\KH\end{matrix}\right\}O_2=KHSO_4\ (\textit{acid salt}).$$

$$\left.\begin{matrix}SO_2\\K_2\end{matrix}\right\}O_2=K_2SO_4\ (\textit{normal salt}).$$

(3.) Similarly, a *tribasic acid* is regarded as formed on a treble water type $\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$; ($\alpha$) *the acid* resulting from the H_3 being replaced by a triatomic compound radical; (β) *the anhydride* by the $2H_3$ being replaced by two atoms of the triatomic radical; and (γ) *the salts* by the displacement of one or more of the hydrogens of the acid by a metal. Thus—

$$(\alpha)\ \left.\begin{matrix}PO\\H_3\end{matrix}\right\}O_3=H_3PO_4\ (\textit{acid}).$$

$$(\beta.)\ \left.\begin{matrix}PO\\PO\end{matrix}\right\}O_3=P_2O_5\ (\textit{anhydride}).$$

$$(\gamma.)\ \left.\begin{matrix}PO\\Na_3\end{matrix}\right\}O_3=Na_3PO_4\ (\textit{salt}).$$

II. Bases.

A Base is "*a compound body capable of being converted into a salt by the action of an acid, and of thereby more or less neutralizing the reactions of the acid.*" Bases may be divided into three classes.

(1.) *Compounds of metals with oxygen* (such as baryta, lime, magnesia). A metal usually forms but one oxide capable of producing salts with acids; but to this general rule there are many exceptions. Thus—

The *protoxide of iron* (FeO) forms salts (e.g., FeO, SO_3) distinguished as protosalts, or more commonly as *ferrous salts*.

The *peroxide of iron* (Fe_2O_3) forms salts (e.g., Fe_2O_3, $3SO_3$) distinguished as *persalts*, or more commonly as *ferric salts*.

(2.) *Compounds of metals with the compound radical hydroxyl* (HO) (*hydroxides*, e.g., sodic hydrate NaHO (soda); potassic hydrate KHO (potash), etc.) A hydroxide consists of one or more water molecules, where one or more of the hydrogens are replaced by a metal. Thus—

$$\left.\begin{matrix}K'\\H\end{matrix}\right\}O=K'HO;\ \left.\begin{matrix}Ca''\\H_2\end{matrix}\right\}O_2=Ca''H_2O_2.$$

The soluble hydroxides are called *alkalies*, and have the power of blueing red litmus.

(3.) *Certain compounds with nitrogen, phosphorus, arsenic, and antimony*, as, for example, ammonia (NH_3).

III. Salts.

A Salt is "*a compound formed by the mutual action of an acid on a base.*" The name given to the salt depends on the base and the acid present. Thus sodic nitr*ate* implies a salt formed by a combination of sodium and nitr*ic* acid; sodic nitr*ite*, a salt formed by a combination of sodium and nitr*ous* acid.

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Varieties of Salts.

(1.) *Haloid Salts. Compounds of a metal with a halogen, or salt radical.* A haloid salt, therefore, contains neither oxygen nor sulphur (*e.g.*, NaCl, KI).

(2.) *Oxy-Salts. Compounds formed from an oxygen acid, by the displacement of all or a part of its hydrogen by a metal or by a compound radical.* Of these we recognize several classes.

(α.) *Normal Salts. A salt where all the displaceable hydrogen of the acid is exchanged for an equivalent amount of a metal or of a positive compound radical.* Thus, for example,

K_2SO_4 from H_2SO_4; $NaNo_3$ from HNO_3; $Ca''_32(PO_4)$ from $2H_3PO_4$.

A *normal* salt was formerly termed a *neutral* salt, that is, a salt which neither reddens blue-litmus nor blues red-litmus. Neutrality, however, depends more on chemical energy than on actual proportion. Thus $ZnSO_4$ reddens *blue* litmus, and Na_2CO_3 blues *red* litmus, whilst other normal salts, such as KNO_3, are strictly neutral. Yet in none of these is there any free acid nor free base present. Litmus being itself a salt consisting of a feeble vegetable acid of a *red* color, combined with a metallic base, the addition of a salt containing a strong acid, may set free the red litmus acid, owing to the greater intensity of the strong acid of the salt for the litmus base, than that possessed by the litmus acid itself. Hence a normal salt may redden blue litmus.

(β.) *Acid Salts. A salt in which the displaceable hydrogen of the acid is only partially exchanged for a metal or positive compound radical.* Acid salts are invariably salts of polybasic acids. All acids, the hydrogen of which plays the part of a true metal atom, and is not simply the hydrogen of water of crystallisation, are, in a sense, true acid salts. Thus—

$KHSO_4$ is derived from H_2SO_4; $KHCO_3$ from H_2CO_3; HNa_2PO_4 from H_3PO_4.

(γ.) *Basic Salts. A salt where the number of bonds of the metal or compound radical exceeds the number of atoms of displaceable hydrogen in the acid.* This implies that the proportion of base present predominates over the acid. Thus—

$HgSO_4,2HgO$ =Turpeth Mineral.
$CuCO_3,CuH_2O_2$ =Malachite.
$2PbCO_3$, PbH_2O_2=White lead.

Here it will be seen that the base is in excess of the acid.

(3.) *Sulpho-Salts.—Compounds analogous to oxysalts, but containing sulphur in the place of oxygen.* Thus—

Sodic sulph-arseniate; $3Na_2S,As_2S_5$, or $2Na_3AsS_4$;
Sodic sulpho-stannate; $2Na_2S,SnS_2$.

(4.) *Double Salts.—Compounds where the displaceable hydrogens of the*

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acid are exchanged by different metals or compound radicals. Thus Rochelle salt is a compound formed from tartaric acid ($H_2C_4H_4O_6$), in which the two atoms of hydrogen are displaced by an atom of sodium and potassium respectively ($KNaC_4H_4O_6$).

Double salts may be formed, and more often are formed, from oxides of different classes. Thus common alum consists of potassic and aluminic sulphate, $K_2SO_4,Al_2 3SO_4 = K_2Al_2 4SO_4$. Double salts may also be formed by a combination of haloid salts. Thus 2 KCl, $PtCl_4$ forms potassic platinic chloride. These combinations are regarded as molecular rather than atomic.

The terms *oxychloride, oxyiodide,* etc., imply compounds formed by the union of one or more molecules of a metallic oxide with one molecule of a chloride or iodide of the same metal. Thus $PbCl_2,7PbO$ = oxychloride of lead (Turner's yellow).

HALOID SALTS (ἅλς the sea).

Definition.—A haloid salt is a compound either of a metal or of a compound radical, capable of acting as a metal (such as NH_4), with a salt radical which may be either simple, like chlorine, or compound, like cyanogen.

Members.—Chlorides, iodides, bromides, fluorides, sulphides, selenides, phosphides, carbides, borides, silicides, cyanides.

I.—Chlorides.

Definition.—Compounds of metals with chlorine (the radical of HCl).

Natural History.—The chlorides are found in all three kingdoms of nature, chiefly in combination with the alkalies. Sodic and potassic chlorides occur in sea water and in rock salt. Mercurous chloride (Hg_2Cl_2) and silver chloride (AgCl) occur as natural minerals.

Preparation.—(1.) By the direct action of chlorine, either (α) on *a metal* ($Mg + Cl_2 = MgCl_2$); or (β) on *a basic oxide,* either in the cold (as AgCl), or when heated to redness, whereby the oxygen of the oxide is expelled; or (γ) on *a heated mixture of carbon and a metallic oxide,* whereby carbonic oxide is evolved ($M_2O + C + Cl_2 = MCl_2 + CO$); or ($\delta$) on *a sulphide,* whereby a chloride of sulphur and a metallic chloride are formed.

(2.) By dissolving a metal in aqua regia (this being in reality the action of nascent chlorine), evaporating the solution to dryness, and redissolving the residue in water (*e. g.,* Au, Pt, etc.).

(3.) By the action of hydrochloric acid gas, either (α) on *a metal* ($Na_2 + 2HCl = 2NaCl + H_2$); or ($\beta$) on *an oxide* ($CuO + 2HCl = CuCl_2 + H_2O$); or ($\gamma$) on *a sulphide* of a metal.

(4.) By dissolving either a metal (*see* page 247), an oxide, a hydrate, or a carbonate of a metal in liquid hydrochloric acid, and

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evaporating. The hydrated chlorides may be prepared by this process. Many hydrated chlorides, however, evolve their chlorine as HCl, when their solutions are evaporated—

$$(MgCl_2 + H_2O = MgO + 2HCl).$$

(5.) The insoluble chlorides may be prepared by adding hydrochloric acid (or a soluble chloride) to a salt of the metal (*e.g.*, AgCl, $PbCl_2$, Hg_2Cl_2).

(6.) A chloride of a metal may sometimes be formed by treating the metal itself with the chloride of another metal, whereby the first metal will appropriate the chlorine of the second metal. Thus, if sodium be heated with magnesic chloride, sodic chloride and free magnesium are produced; or, if potassium be heated with uranous chloride, potassic chloride and free uranium are formed. (Similarly, $SnCl_4$, $SbCl_3$, or $BiCl_3$ may be prepared by heating Sn, Sb, or Bi with $HgCl_2$.)

Varieties of Chlorides.—(1.) *Subchlorides* ($'M'_2Cl_2$) $\left\{\begin{matrix}MCl\\MCl\end{matrix}\right.$; as *e.g.*, *Mercurous chloride* (Hg_2Cl_2), *Cuprous chloride* (Cu_2Cl_2).

(2.) *Monochlorides* (M'Cl as KCl); *Dichlorides* ($M''Cl_2$ as $Ca''Cl_2$); *Trichlorides* ($M'''Cl_3$ as $Sb'''Cl_3$); *Tetrachlorides* ($M^{iv}Cl_4$ as $Pt^{iv}Cl_4$); *Pentachlorides* (M^vCl_5 as Sb^vCl_5); *Hexachlorides* ($M^{vi}Cl_6$ as $Mo^{vi}Cl_6$).

(3). *Sesquichlorides* ($'M'''_2Cl_6$) $\left\{\begin{matrix}MCl_3\\MCl_3\end{matrix}\right.$; as *Ferric chloride* ($Fe_2Cl_6$).

One metal is often found to combine with chlorine in more than one proportion. Thus—

(α.) $FeCl_2$, Ferrous chloride; Fe_2Cl_6, Ferric chloride.
(β.) $PtCl_2$, Platinous chloride; $PtCl_4$, Platinic chloride.

Properties.—(α.) *Sensible and Physical.* The *colors* of the chlorides are various; the alkaline chlorides are white. Their *taste* is mostly saline or bitter. Generally they have no odor. They usually crystallize in cubes, but sometimes in square prisms (calomel), sometimes in rhombohedra ($CaCl_2$), and sometimes in oblique prisms ($BaCl_2$). Some chlorides are soft, as argentic chloride (horn silver), and those chlorides known as *metallic butters* ($SbCl_3$, $SnCl_2$); whilst some are liquid, and are known as *metallic oils* ($SbCl_5$, $AsCl_3$). When exposed to the air they are mostly deliquescent.

Action of Heat.—(α.) They are all fusible and volatile. (1.) Some volatilize at about 212° F. (100° C.), as, *e.g.*, Al_2Cl_6, Fe_2Cl_6, $AsCl_3$, etc.; (2.) some at a red heat, as $NiCl_2$; (3.) but most of them at a higher temperature.

(β.) Some are *partly* decomposed by heat. Thus $2CuCl_2$ becomes, at a red heat, $Cu_2Cl_2 + Cl_2$.

(γ.) Some are *completely* decomposed by heat; as, *e.g.*, $PtCl_4$, $PdCl_2$, $AuCl_3$.

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(δ.) Many (the chlorides of the noble metals excepted) when *ignited in air or oxygen* are decomposed, with the formation of an oxide and the escape of chlorine.

(ϵ.) Many (the chlorides of the alkaline metals and those of barium and mercury excepted) when *heated in the presence of water*, form oxides and hydrochloric acid. [N.B. Bismuth forms an oxychloride.]

(ζ.) All (excepting the chlorides of the alkalies and alkaline earths) when *ignited in a free current of hydrogen* are decomposed, hydrochloric acid being formed.

Solubility in Water.—The chlorides are generally deliquescent, and very soluble in water; $PbCl_2$ is, however, only very slightly soluble, whilst AgCl, Hg_2Cl_2, AuCl, and $PtCl_2$ are insoluble.

Solubility in Alcohol and Ether.—Most chlorides are very soluble in alcohol, but NaCl is only slightly soluble, and some others, as KCl, $BaCl_2$, AgCl, and Hg_2Cl_2 are insoluble. Excepting those of the noble metals, the chlorides are insoluble in ether.

Action of Light.—Some chlorides, as, *e.g.*, AgCl, are decomposed by exposure to light.

Action of Electricity.—The chlorides are mostly decomposed by electricity.

(β.) *Chemical.*—The chlorides have generally an acid, but never an alkaline reaction. The chlorides of the alkaline metals are neutral.

Water dissolves most chlorides without decomposition, but there are certain exceptions, such as, *e.g.*, $SbCl_3$, $BiCl_3$, $SnCl_2$, which form hydrochloric acid, and an oxychloride when treated with water ($BiCl_3 + H_2O = 2HCl + BiClO$).

Acids, especially when heated, decompose the chlorides (argentic and mercurous chlorides excepted), setting free hydrochloric acid. All the soluble chlorides, when heated with sulphuric acid and manganic peroxide, evolve chlorine, which is also commonly given off when they are heated with nitric acid. The chlorides of the metals combine with each other ($2KCl,PtCl_4$), also with the chlorides of the non-metals (KCl,ICl_3), and also with metallic oxides, forming oxychlorides ($3HgO,HgCl_2$).

Tests.—*For the soluble chlorides.*

(α.) *Argentic nitrate:* a white precipitate of AgCl, insoluble in nitric acid, soluble in ammonia and in potassic cyanide. The precipitate blackens on exposure to light.

(β.) *Mercurous nitrate:* a white precipitate of mercurous chloride (calomel) [$Hg_2(NO_3)_2 + 2NaCl = 2NaNO_3 + Hg_2Cl_2$] soluble in chlorine water, and blackened by ammonia.

(γ.) *Plumbic acetate* gives, in strong solutions, a white crystalline precipitate of plumbic chloride ($PbCl_2$), soluble in excess of water.

(2.) *For the insoluble chlorides* (AgCl, Hg_2Cl_2, $PbCl_2$).

[Note.—$PbCl_2$ is readily soluble in boiling water.]

Boil the insoluble chloride in a pure solution of potassic hydrate,

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filter off the undissolved oxide, acidulate the solution with nitric acid, and test with argentic nitrate for chlorine.

Estimation of Chlorides.—100 grains of AgCl=24·74 of chlorine.

Uses.—Common salt in diet, etc. The mercury and other chlorides are used in medicine.

II. Iodides.

Definition.—Compounds of metals with iodine (the radical of HI).

Natural History.—The iodides are found in all three kingdoms of nature, but chiefly in sea and in mineral waters, and in the plants and animals living therein. Argentic iodide is a natural mineral.

Preparation.—1. (α.) By the direct union of iodine and the metal (*e.g.*, HgI_2; AsI_3); or (β) by passing iodine vapor over metallic oxides, either alone or mixed with carbon.

2. By the action of hydriodic acid on metals (as Hg), or on the oxides, the hydrates, and on certain salts (as AgCl) of the metals.

3. By the action of iodine on a solution of the alkalies and alkaline earths, whereby an iodide and an iodate are formed, the iodate on ignition becoming an iodide (Process of P.B. for making KI).

4. The insoluble iodides may be prepared by adding a metallic salt to a solution of potassic iodide (HgI_2, AgI, PbI_2).

Properties.—The iodides are closely allied to the chlorides.

(α.) *Sensible and physical.* The alkaline iodides are white, but the remaining iodides, as HgI_2, PbI_2, etc., are most often colored. They commonly crystallize in cubes. They are mostly soluble both in alcohol and in water; but HgI_2, AgI, PbI_2, BiI_3, PdI_2, are insoluble in water.

Action of heat. The iodides are less fusible and less volatile than the corresponding chlorides.

(1.) Most iodides are fusible, and many are volatile at high temperatures.

(2.) When *ignited in air or oxygen* they are usually decomposed, iodine being set free, and an oxide of the metal formed (Exceptions—KI, NaI, PbI_2, BiI_3). In the case of AuI_3, AgI, PtI_4, PdI_2, the metal is reduced and iodine is set free.

(3). When *heated in the presence of water*, they are mostly decomposed into hydriodic acid and an oxide of the metal.

Light acts on many of the iodides. Thus AgI is blackened; Hg_2I_2 is decomposed into Hg and HgI_2.

(β.) *Chemical.* The iodides are decomposed (1) by *chlorine* and *bromine*, iodine being set free, (2) also by *hydrochloric acid*, hydriodic acid, and a chloride of the metal being formed, (3) also by *sulphuric, nitric, and nitrous acids*, and (4) also when heated with sulphuric acid and manganic peroxide, when iodine is evolved. The iodides of those metals which form acids with oxygen, viz., SnI_4, SbI_3, TeI_4, AsI_3, are decomposed by water, and an oxide of the metal precipitated.

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The iodides readily combine amongst themselves; also with oxides, forming oxy-iodides, and with chlorides (SnI_2SnCl_4). Moreover, the metallic iodides absorb ammonia in definite proportions.

Tests for Iodides.—(1.) *Starch water*, with a trace either of chlorine water or of nitric or sulphuric acids (added to liberate the iodine) forms, with a soluble iodide, the *blue iodide of starch*.

(2.) *Mercuric chloride* ($HgCl_2$), a scarlet ppt. of *mercuric iodide* (HgI_2), soluble in excess both of the iodide and of the test solution.

(3.) *Plumbic acetate*, a yellow ppt. of *plumbic iodide* (PbI_2), soluble in hot water, and precipitated in yellow crystalline scales on cooling.

(4.) *Argentic nitrate*, a buff ppt. of *argentic iodide* (AgI), insoluble in nitric acid, sparingly soluble in ammonia, soluble in potassic cyanide.

(5.) *A mixture of cupric sulphate and ferrous sulphate*, a white ppt. of *cuprous iodide* (Cu_2I_2).

(6.) *Salts of Palladium*, a brown ppt. of *Palladious iodide* (PbI_2), insoluble in water. (The $PdCl_2$ is freely soluble.)

Estimation.—If chlorides and bromides be absent, the iodine may be estimated as AgI (100 grs.=54·04 I); but if chlorides or bromides be present, it must be precipitated as PdI_2 (100 grs.=70·457 I).

Uses.—Chiefly in *medicine*. KI (a solution of which is used as a solvent for iodine), CdI_2 or FeI_2 (prepared by direct union), PbI_2 (prepared by the action of KI on $Pb2NO_3$), and S_2I_2 are officinal.

III.—Bromides.

Definition.—Compounds of metals with bromine (the radical of HBr).

Natural History.—Bromides are found in sea-water and in saline springs. Argentic bromide occurs as a natural mineral.

Preparation.—Their preparation corresponds to that of the iodides.

Varieties.—These correspond to the chlorides.

Properties.—(α.) *Physical.*—They are all solid. They may all be fused and volatilized, excepting $AuBr_3$ and $PtBr_4$, which are decomposed by heat.

(β.) *Chemical.*—When heated in chlorine, the bromides are converted into chlorides. Heated with *hydrochloric acid*, hydrobromic acid is evolved. They are all decomposed by sulphuric and by nitric acids, hydrobromic acid being set free, which is itself decomposed if the sulphuric or the nitric acid be in great excess, when free bromine is evolved, together with SO_2 or N_2O_4. By the joint action of sulphuric acid and manganic peroxide, the bromides evolve free bromine. The bromides combine amongst themselves, as well as with oxides, to form oxy-bromides, and with sulphides. They also freely absorb ammonia.

Tests for Bromides.—(1.) Add to a solution of a bromide a little

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chlorine water or a *few bubbles of chlorine* (avoiding excess). The liquid becomes red, from bromine being set free. Divide this into two parts (α and β).

(α.) *Shake up one part with ether or with carbonic disulphide*, by which means the bromine will be dissolved out of the solution.

(β.) *Add starch water*, when the yellow bromide of starch will be formed.

(2.) *Argentic nitrate;* a whitish-yellow ppt. of *argentic bromide* (AgBr), insoluble in hot nitric acid, sparingly soluble in ammonia.

(3.) *Mercurous nitrate* ($(Hg_2)''2NO_3$); a yellowish-white ppt. of *mercurous bromide* (Hg_2Br_2), soluble in chlorine water, bromine being set free.

(4.) *Plumbic acetate;* a white ppt. of *plumbic bromide* ($PbBr_2$), less soluble in water than $PbCl_2$, soluble in dilute nitric acid.

(5.) *Palladic nitrate* (*in solutions not containing chlorides*); a black ppt. of *palladic bromide.*

Estimation of Bromides.—In the absence of chlorides, the bromine may be estimated as AgBr (100=42·55 Br).

Uses.—Chiefly in *medicine.* NH_4Br (prepared by the action of HBr on NH_3), $FeBr_2$ (prepared by direct union), KBr (prepared as KI) (page 259), are officinal.

IV.—Fluorides.

Definition.—Compounds of metals with fluorine (the radical of HF).

Natural History.—The fluorides are abundant in the mineral kingdom, and are also found in animals and vegetables.

Preparation.—(1.) By the action of hydrofluoric acid on a metal or on its oxide.

(2.) The insoluble fluorides may be prepared by mixing a solution of a salt of the metal with potassic or with sodic fluoride.

Properties.—(α.) *Physical.* They are mostly solid, and crystallise in cubes. Silicic fluoride (SiF_4) is a gas.

Action of Heat.—All the fluorides fuse by heat (*fluo*, to flow). Many, such as SbF_3, AsF_3, Cr_2F_6, HgF_2, SnF_4, ZnF_2, are volatile. They are not decomposed, either when ignited alone or with carbon.

Action of Water.—A few fluorides are freely soluble (as AgF, SnF_4), their solutions corroding glass; some are sparingly soluble (as KF, NaF, Fe_2F_6), but the majority are insoluble.

(β.) *Chemical.*—The fluorides of ammonium, sodium, and potassium have an alkaline reaction. When ignited in a current of steam they form oxides of the metals and hydrofluoric acid; when ignited in a current of chlorine many of them are decomposed, and a chloride of the metal produced.

They are not readily acted on by nitric acid. With sulphuric acid

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they evolve hydrofluoric acid, leaving a metallic sulphate. They exhibit a marked tendency to combine amongst themselves, and also with another molecule of the acid (HF,KF).

Tests.—(1.) The *fluorides* gives precipitates with salts of lead, barium, and magnesium, but give no precipitate with nitrate of silver.

(2.) A *salt of calcium* gives an almost invisible jelly-like precipitate of CaF_2, which is rendered more apparent by the addition of ammonia. The precipitate is not very soluble in acids, but when treated with sulphuric acid, fluorine is evolved, which acts on glass.

Estimation of Fluorides.—Mix the fluorides with powdered glass and sulphuric acid, and distil into an ammonia solution. The SiF_4 which comes over is decomposed by the water. Evaporate the contents of the receiver to dryness, by which means the silica will be rendered insoluble. Dissolve out the ammonic fluoride with water, and weigh the silica. (Wilson.)

Uses.—Chiefly for glass etching.

V.—Sulphides (Hydrosulphates).

Definition.—Compounds of metals with sulphur (the radical of H_2S).

Natural History.—Found largely in the mineral kingdom.

Preparation.—(1.) By the direct union of sulphur with a metal (such as CuS, FeS, PbS, SnS), or with a metallic oxide. In this latter case, however, a variable proportion of sulphate is formed simultaneously.

(2.) By heating a metallic oxide in a current of H_2S or CS_2 vapor. In this way titanic sulphide may be prepared from titanic anhydride ($TiO_2 + CS_2 = TiS_2 + CO_2$).

(3.) By the ignition (reduction) of *sulphates*, either (α) with *carbon* or with organic substances generally (as, *e.g.*, in the preparation of sulphides of the alkalies and alkaline earths) when CO is evolved ($K_2SO_4 + 4C = K_2S + 4CO$); or—

(β.) In *a current of hydrogen*, as, *e.g.*, in the preparation of the protosulphides of the alkalies, and the subsulphides of other metals, when some of the sulphur volatilizes.

(4.) By the precipitation of metallic solutions, either (α.) by *sulphuretted hydrogen*, the solution of the salt of the metal being acid in the case of the formation of Sb_2S_3, SnS_2, As_2S_3, Au_2S_3, PtS_2; or either acid or neutral in the case of PbS, HgS, Ag_2S, Bi_2S_3, CuS, CdS;—

(β.) By an *alkaline sulphide*, *e.g.*, ZnS, MnS, etc., or—

(γ.) By a *hyposulphite*, added to an acid solution. In this case hyposulphurous acid is set free, and is immediately decomposed into sulphur and sulphurous anhydride ($S_2O_2 = S + SO_2$), which sulphur combines with the metal present to form a sulphide. In this way antimony vermilion (Sb_2S_3) is prepared from an acid solution of the chloride of

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antimony by the action upon it of the hyposulphite of lime derived from alkali waste.

Properties.—(*a.*) *Physical.* All the sulphides are solid, and many are crystalline (cubic). They are of various colors; thus, ZnS is *white;* MnS is *flesh red;* CdS, As_2S_3, SnS_2, are *yellow;* SnS is *chocolate;* whilst the rest are more or less black. Many have a metallic lustre. The sulphides of the alkali metals, and those of barium and strontium are freely soluble in water; calcic and magnesic sulphides are slightly soluble, whilst the rest are insoluble. They are generally fusible and volatile. The further action of heat upon them will be studied under the chemical properties.

(*β.*) *Chemical.*—There is a close relationship between the oxides and the sulphides. As oxygen often combines with a metal in more than one proportion, forming protoxides and peroxides, so sulphur forms protosulphides, as ferrous sulphide (FeS), and persulphides as ferric sulphide (Fe_2S_3). This law, however, is not absolute. There is no sulphide, *e.g.*, corresponding to MnO_2, and no oxides corresponding to K_2S_3 and K_2S_5.

Action of air.—On exposure to air, even at common temperatures, some sulphides become sulphates ($CuS+O_4=CuSO_4$), an action utilized in the separation of copper from tin ores. Some, as, *e.g.*, those metallic sulphides which form alkaline oxides, when exposed to moist air, yield, in the first instance, a mixture of an oxide with a bisulphide, and afterwards of an oxide with a hyposulphite, this latter being formed by the further oxidation of the bisulphide. Thus—

(*a.*) $4Na_2S + O_2 = 2Na_2O + 2Na_2S_2$.
Sodic sulphide + Oxygen = Sodic oxide + Sodic bisulphide.

(*β.*) $2Na_2S_2 + 3O_2 = 2Na_2S_2O_3$.
Sodic bisulphide + Oxygen = Sodic hyposulphite.

Some sulphides, when exposed to the air, part with their sulphur and become oxides. In this way the spent oxide of gas-works is revivified. Thus—

$4FeS + 3O_2 = 2Fe_2O_3 + 2S_2$.
Ferrous sulphide + Oxygen = Ferric oxide + Sulphur.

Some sulphides combine with oxides to form *oxy-sulphides* ($Sb_2O_32Sb_2S_3$), and some with carbonic disulphide to form *sulpho-carbonates* (K_2S,CS_2).

Action of heat.—(*a.*) The protosulphides, if air be excluded, are not decomposed by heat.

(*β.*) Heated in the presence of air, some sulphides are *partially decomposed,* as *e.g.*, FeS_2 becomes FeS. Some are *changed into sulphates,* as *e.g.*, in the formation of zincic sulphate from blende ($ZnS+2O_2=ZnSO_4$). In some the sulphur is expelled as sulphurous anhydride, and *an oxide of the metal formed,* as *e.g.*, in extracting copper from the ore ($Cu_2S+2O_2=2CuO+SO_2$). In some *the metal is*

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entirely reduced, as *e. g.*, Au_2S_3, PtS_2; whilst in some a mixture of the reduced metal and a sulphate is formed (Ag).

(γ.) Some sulphides sublime when heated, as, *e. g.*, As_2S_3 (*orpiment*), and HgS (*cinnabar*).

(δ.) Some sulphides are reduced when *heated in a stream of hydrogen*, as *e. g.*, Ag_2S, CuS, Bi_2S_3, SnS_2, Sb_2S_3.

(ε.) Some sulphides are reduced when *heated with iron*, as *e. g.*, PbS, SnS_2.

(ζ.) All sulphides are decomposed when *heated in a stream of chlorine*, chloride of sulphur and a chloride of the metal being formed.

Action of acids.—Cold dilute sulphuric acid and also hydrochloric acid dissolve most of the sulphides, sulphuretted hydrogen being evolved. With HCl a chloride of the metal is formed ($Sb_2,S_3+6HCl=2SbCl_3+3H_2S$). The sulphides of cobalt, of nickel, and of platinum are not acted upon by hydrochloric acid unless the sulphides be boiled in the acid. All the sulphides (excepting mercuric sulphide) are decomposed by nitric acid, sulphuric acid and a nitrate of the metal being formed. They are all freely attacked by nitro-hydrochloric acid.

Action of sulphuretted hydrogen. Sulph-hydrates.—When sulphuretted hydrogen is passed through a solution of the sulphide of an alkali or of an alkaline earth, a soluble *sulph-hydrate, hydrosulphide* or *hydric-sulphide*, as it is called, is formed ($K_2S+H_2S=2KHS$). This compound holds an intermediate position between sulphuretted hydrogen and the ordinary sulphide, and closely corresponds in constitution to a hydrate. The ammonic hydric-sulphide (NH_4HS) belongs to this class. The sulph-hydrates smell of sulphuretted hydrogen, which is set free when they are acted upon by a metallic salt, a reaction which serves to distinguish them from simple sulphides—

$$(2NH_4HS+MnSO_4=(H_4N)_2SO_4+MnS+H_2S).$$

Sulphides (like oxides) are both basic and acid. Thus, an acid sulphide (as As_2S_5) can react on a basic sulphide (as Na_2S) to form a new and double compound, as, *e. g.*, ($3Na_2S,As_2S_5$.) Most of these double sulphides are soluble in water. The importance of this fact in analysis is manifest, inasmuch as we are often enabled in a mixed precipitate of metallic sulphides to dissolve out one sulphide by the addition of a sulphide of an alkali metal (as NH_4HS), and so effect its separation from a second sulphide.

Action of alkalies and alkaline carbonates.—The sulphides are decomposed by fusion with alkaline carbonates or with hydrated alkalies.

Tests for the Sulphides:—

(1.) Heated with the blowpipe they emit an odor of SO_2.

(2.) Moistened with HCl they evolve H_2S, which blackens lead paper.

(3.) *Sodic nitro-prusside* gives a purple color with a neutral or an alkaline solution of a sulphide.

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Estimation of Sulphides.

(1.) By first oxidizing the sulphur to sulphuric acid by aqua regia or by chlorine, and afterwards precipitating the sulphuric acid with BaCl (100 $BaSO_4$=13·73 of S).

(2.) To determine the quantity of free H_2S or of a soluble sulphide present in solution, mix the solution with a little starch water and acidulate with acetic acid; add to this a standard solution of iodine in potassic iodide, until the blue iodide of starch is formed.

The H_2S converts the iodide into HI, whilst the sulphur is set free ($2H_2S+2I_2=4HI+S_2$).

FORMATION OF SULPHIDES BY H_2S.

Class I.—*Metals not precipitated by* H_2S, *their sulphides being soluble in water.**
Examples (K, Na, Li, Ba, Sr, Ca, Mg).

Class II.—*Metals precipitated by* H_2S *in an* ACID *solution, but not in an* ALKALINE *solution*, their sulphides forming double and soluble salts, with the alkalies.
Hence: *they are soluble in, and not precipitated by an excess of ammonic sulphide.*
Examples (Sb, Sn, As, Au, Pt).

Class III.—*Metals precipitated by* H_2S *in an* ALKALINE *solution, but not in an* ACID *solution*, the acid dissolving the sulphide. They do not form double compounds with the alkalies.
Hence: *they are insoluble in, and precipitated by, ammonic sulphide.*
Examples (Ni, Co, Zn, Mn, Fe).

Class IV.—*Metals precipitated by alkaline sulphides as oxides and not as sulphides.*
Examples (Cr, Al).

Class V.—*Metals precipitated by* H_2S, *either in an acid or in an alkaline solution.*
Hence: *they are precipitated equally by* H_2S *and by ammonic sulphide.*
Examples (Pb, Hg, Ag, Bi, Cu, Cd).

VI. and VII.—Selenides and Tellurides.

Definition.—Compounds of metals with selenium (the radical of selen-hydric acid or selenetted hydrogen, H_2Se) and with tellurium (the radical of hydro-telluric acid or telluretted hydrogen, H_2Te).

These salts are closely allied to sulphides.

The presence of selenium may be known by the peculiar smell emitted when the selenide is heated in the reducing flame of the blowpipe.

VIII.—Phosphides.

Definition.—Compounds of metals with phosphorus.

Natural History.—The phosphides are never met with native.

Preparation.—In one or other of the following ways.

(1.) By the direct union of phosphorus and a metal (Au,Pt).

(2.) By igniting a metal with phosphoric anhydride (or with a phosphate) and carbon.

(3.) By passing the vapor of phosphorus over a heated oxide (CaP).

* Baudrimont (J. Pharmac. Chem. Series IV. xxii. 15-19) points out that a 40° Baumé solution of sodic, and probably of potassic hydrate at 15° C., is precipitated by H_2S, the precipitate having the composition Na_2S, $9H_2O$. It is very soluble in water.

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(4.) By passing phosphoretted hydrogen through a solution of a metallic salt.

Properties.—The phosphides are brittle solids, with a metallic lustre. They are decomposed by heat, especially in the presence of air, with the formation of either a phosphate or phosphoric anhydride and the free metal. The phosphides of the alkalies and of the alkaline earths decompose water, generating self-inflammable phosphoretted hydrogen.

IX.—Carbides.

Definition.—Compounds of metals with carbon.

The carbides of iron are the only carbides of importance. Manganese, palladium, etc., also form carbides. The carbides are usually more fusible than the metals.

X. and XI.—Silicides and Borides.

Definition.—Compounds of metals with silicon and boron.

They are of very little importance.

The **Cyanides** will be considered under cyanogen.

OXYSALTS.

Definition.—Salts formed from an oxygen acid by the displacement of all, or of a part of its hydrogen by a metal, or by a compound radical.

I.—Sulphates.

Definition.—Salts formed from sulphuric acid H_2SO_4 (SO_2Ho_2).

Natural History.—The sulphates are found in the animal, in the vegetable, and in the mineral kingdoms.

Varieties and Constitution.—(*α.*) *Normal Sulphates* (M_2SO_4 or SO_2Mo_2). A sulphate where all the displaceable hydrogen of the H_2SO_4 is exchanged for a metal, etc., as K_2SO_4; $Ba''SO_4$; $Pb''SO_4$, etc.

(*β.*) *Acid Sulphates* ($MHSO_4$ or SO_2MoHo). A sulphate where the displaceable hydrogen of the H_2SO_4 is only partially exchanged for a metal, etc., as $HNaSO_4$ (hydric sodic sulphate, also called bisulphate).

(*γ.*) *Basic Sulphates.* A sulphate where the base present is in excess of the acid, as *e.g.*, Hg''_3SO_6 (turpeth mineral).

(*δ.*) *Double Sulphates* are formed by the combination of two sulphates, as *e.g.*, in the alums (K_2SO_4,$Al_2 3SO_4 + 24$ *Aq.*).

Many sulphates are anhydrous (K, Ba, Sr, Pb, Ag); some contain 5 molecules of water (Cu); most contain 7 molecules (Mg, Zn, Fe, Co); and some 10 molecules (Na). The alums contain from 12 to 27 molecules.

Preparation.—(1.) By the artificial or spontaneous oxidation of

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sulphides. Thus FeS and CuS, by roasting or by exposure to weather, become $FeSO_4$ and $CuSO_4$.

(2.) By the action of sulphuric acid on a metal or on an oxide, carbonate, or other salt of a metal.

(N.B.—Sulphuric acid displaces all acids that boil at a lower temperature than itself).

(α.) The action of a *dilute acid* on metals is accompanied with the evolution of hydrogen.

(β.) The action of a *concentrated acid* and *heat* on the metals is accompanied with the evolution of sulphurous anhydride (*e. g.* Cu, Ag, Sb, Sn, Hg).

(γ.) Action on *oxides* (*e. g.* $ZnO+H_2SO_4=ZnSO_4+H_2O$; $2MnO_2+2H_2SO_4=2MnSO_4+2H_2O+O_2$).

(δ.) Action on *sulphides* (*e. g.* $FeS+H_2SO_4=FeSO_4+H_2S$).

(ϵ.) Action on *hydrates* (*e. g.* $MnH_2O_2+H_2SO_4=MnSO_4+2H_2O$).

(ζ.) Action on *carbonates* (*e. g.* $Na_2CO_3+H_2SO_4=Na_2SO_4+H_2O+CO_2$.)

(η.) Action on *chlorides* (*e. g.* $2NaCl+H_2SO_4=Na_2SO_4+2HCl$).

(3.) By the action of sulphurous anhydride on metallic peroxides—

$$SO_2+PbO_2=PbSO_4.$$

(4.) The insoluble sulphates are formed by adding a soluble sulphate to a soluble salt of the metal. Thus—

$$BaCl_2+H_2SO_4=BaSO_4+2HCl.$$

(N.B.—The sulphates often occur as residues in the preparation of volatile acids. Thus K_2SO_4 is obtained in the nitric acid, and Na_2SO_4 in the hydrochloric acid manufacture).

Properties.—(α.) *Physical.*—The sulphates are all crystallizable solids. The crystals are of different shapes; viz., *cubic*, as in the alums; *singly oblique*, as in the sulphates of sodium, iron, and cobalt, and also in the non-aluminous double sulphates; *doubly oblique*, as in the sulphates of copper and manganese. They are generally white, but some few are colored. Their taste is usually a saline-bitter and astringent. They have no odor.

Action of heat.—(α). The normal sulphates of the alkalies and of the alkaline earths, and plumbic sulphate, are not decomposed by heat.

(β.) The sulphates of Mg, Mn, Zn, Cd, Ni, Co, and Cu are decomposed by an intense heat, SO_2 and O being evolved ($CuSO_4=CuO+SO_2+O$). (Thus, $ZnSO_4$ has been suggested as a source of oxygen.)

(γ.) The remaining sulphates are decomposed easily when heated, sulphuric anhydride being evolved in the case of the sulphates of the noble metals, and sulphurous and sulphuric anhydrides in the case of the remainder ($2FeSO_4=Fe_2O_3+SO_2+SO_3$).

The sulphates are mostly soluble in water, whilst many are soluble in alcohol.

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(β.) *Chemical.*—All the sulphates redden litmus, except the normal sulphates of the alkalies and alkaline earths.

Heated with carbon or with hydrogen, they may all be decomposed. Different reactions occur as follows :—

(α.) In some cases, as with the sulphates of the alkalies and alkaline earths, a sulphide remains, CO, H_2O, or H_2S being evolved* ($K_2SO_4+C_4=K_2S+4CO$; $K_2SO_4+4H_2=K_2S+4H_2O$).

(β.) Sometimes an oxide is formed (Mg, Zn).

(γ.) Sometimes an oxy-sulphide is formed (Sb, Mn).

(δ.) Sometimes the metal is reduced (Cu, Hg, Bi, Ag, and the noble metals).

[Note that in those cases where a sulphide is formed from a sulphate by heating with carbon (α), (*e. g.*, $BaSO_4+4C=BaS+4CO$), the presence of the sulphate may be known by moistening the resulting sulphide with HCl, and testing for H_2S with lead paper.]

Action of acids.—*Nitric acid* and *hydrochloric acid* act on the neutral alkaline sulphates, forming acid sulphates and chlorides respectively. The *fixed acids*, such as boric acid and phosphoric acid, when fused with the sulphates, decompose them, liberating sulphuric anhydride (*see* page 7).

Action of water.—The sulphates generally are soluble in water, but—

(α.) The basic sulphates, with $BaSO_4$, $PbSO_4$, and $Sn2SO_4$ are insoluble.

(β.) $SrSO_4$, $CaSO_4$, Ag_2SO_4 are nearly insoluble.

(γ.) And $HgSO_4$ is decomposed by the action of water into "turpeth mineral" ($2HgO,HgSO_4$), a similar result occurring in the case of the sulphates of bismuth and antimony.

All the insoluble sulphates are decomposed when boiled in a solution of sodic carbonate, a soluble sulphate and an insoluble carbonate being formed.

Organic matter also decomposes the sulphates.

Tests and Estimation of Sulphates.—(A.) *Soluble sulphates :*—

(1.) A *soluble barium salt;* a white ppt. of $BaSO_4$, insoluble in nitric acid. 100 grs. $BaSO_4$=42grsH_2SO_4.

(2.) A *soluble lead or lime salt;* a white ppt. of $PbSO_4$ or $CaSO_4$.

(B.) *Insoluble sulphates :*—

(1.) Fuse the sulphate with a mixture of sodic and potassic carbonates, digest the residue with water, and test the filtrate for a soluble sulphate with $BaCl_2$.

Or, (2.) Boil the sulphate in a solution of sodic carbonate, and test the filtrate for a soluble sulphate.

* NOTE.—In waters containing calcic sulphate and organic matter, a calcic sulphide is formed, even at ordinary temperatures, by the action of the organic matter on the sulphate. The sulphide is decomposed by the carbonic acid, H_2S being set free, which imparts to the water an unpleasant taste.

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Or, (3.) Fuse the insoluble sulphate, mixed with charcoal and sodic carbonate, on charcoal with the blow-pipe. Touch the residue with a drop of acid, when H_2S will be evolved from the sulphide formed.

Uses.—Plaster of Paris ($CaSO_4$) is used in the arts. The sulphates are largely used in medicine, especially *Epsom salts* ($MgSO_4,7H_2O$), *Glauber's salts* ($Na_2SO_4,10H_2O$), *Ferrous sulphate* or *green vitriol* ($FeSO_4,7H_2O$), *Zincic sulphate* or *white vitriol* ($ZnSO_4,7H_2O$).

ALLIES OF THE SULPHATES.

Selenates (from *selenic acid*, H_2SeO_4, or $\mathbf{Se}O_2Ho_2$); *Chromates* (from *chromic acid* H_2CrO_4, or $\mathbf{Cr}O_2Ho_2$); *Manganates* (from *manganic acid*, H_2MnO_4, or $\mathbf{Mn}O_2Ho_2$); *Tungstates* (from *tungstic acid*, H_2WO_4, or $\mathbf{W}O_2Ho_2$); *Molybdates* (from *molybdic acid*, H_2MoO_4 (?), or $\mathbf{Mo}O_2Ho_2$(?)); *Tellurates* (from *telluric acid*, H_2TeO_4, or $\mathbf{Te}O_2Ho_2$).

II.—Selenates.

Definition.—Salts formed from selenic acid, H_2SeO_4 ($\mathbf{Se}O_2Ho_2$).

The selenates are closely allied to the sulphates. They are decomposed when boiled with hydrochloric acid, chlorine being evolved and selenic acid liberated. This is first converted into selenious acid, which is immediately reduced by the sulphurous acid, and selenium deposited.

Tests.—(1.) Salts of *barium*, *strontium*, and *lead;* white ppts. of $BaSeO_4$, $SrSeO_4$, $PbSeO_4$ respectively, insoluble in dilute nitric acid.

(2.) *Baric selenate* may be known from *baric sulphate* by the reaction mentioned above with hydrochloric acid, and also by its emitting the characteristic selenium odor when heated on charcoal with the blow-pipe.

III. - Chromates.

Definition.—Salts formed from chromic acid (H_2CrO_4 or $\mathbf{Cr}O_2Ho_2$).

Both *normal* (M'_2CrO_4), *acid* and *basic* chromates are known. They are all more or less of a yellow or red color. With potash, chromic acid forms four salts; viz.—(1) K_2O,CrO_3 (chromate), (2) $K_2O,2CrO_3$ (bichromate), (3) $K_2O,3CrO_3$ (trichromate), (4) $K_2O,4CrO_3$ (tetrachromate).

They are mostly very soluble in dilute nitric acid, and more or less soluble in water, excepting lead chromate, $PbCrO_4$ (chrome yellow), argentic chromate, Ag_2CrO_4, and the basic chromates, which are insoluble. The chromates are usually decomposed by heat. They are not acted upon by sulphuretted hydrogen, but the green chromic hydrate (Cr_26HO) is precipitated when they are treated with ammonic sulphide, or with the caustic alkalies or their carbonates, in which latter, excepting in the case of ammonic carbonate, they are soluble in an excess.

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Tests.—(1.) Salts of *silver* give a crimson ppt. (Ag_2CrO_4); salts of *barium* and *lead*, yellow ppts. ($BaCrO_4$, $PbCrO_4$); and *mercurous salts*, a brick-red ppt. (Hg_2CrO_4). These precipitates are soluble in nitric acid, and insoluble in acetic acid.

(2.) Mix the dry chromate with two or three drops of sulphuric acid in a test-tube, and apply heat, when chloro-chromic anhydride (CrO_2Cl_2) is set free, and may be known by the red fumes that condense in the glass.

(3.) The insoluble chromates must be ignited on platinum foil with a mixture of nitre and an alkaline carbonate, by which means a soluble alkaline chromate is obtained ($KNaCrO_4$). The residue is to be dissolved in water, neutralized with acetic acid, and tested as above.

(4.) Chromates (and all chromium salts) impart an emerald green color to the borax bead.

IV.—Manganates.

Definition.—Salts formed from manganic acid (H_2MnO_4 or $\mathbf{Mn}O_2Ho_2$).

Preparation.—By the action of heat, in air or oxygen, on a mixture of manganic peroxide with caustic potash, or baryta, or other substance, according to the salt required.

Properties.—The manganates are colored and unstable salts. They are soluble in water containing a free alkali. In common water, however, and more particularly if it contains a trace of acid (even of free carbonic acid), the salt is decomposed into manganic peroxide and a permanganate ($3K_2MnO_4 + 2H_2O = K_2Mn_2O_8 + MnO_2 + 4KHO$). A manganate solution is decomposed by boiling, the solid salt being also decomposed by heat with the evolution of oxygen. The manganates are decomposed by all acids;—with sulphurous, phosphorous, and hypophosphorous acids they are reduced to manganous salts, whilst with sulphuric acid, permanganates are formed. All organic matter, (*e. g.*, a filter paper) deoxidizes them, setting free the brown manganic oxide (Mn_2O_3). The presence of alkalies renders the manganates more stable.

Uses.—The manganates are employed as disinfectants, owing to the readiness with which they yield oxygen to organic matter. "Condy's green disinfecting fluid," is a solution of sodic manganate (Na_2MnO_4) dissolved in potash. It turns red (a permanganate being formed) on the addition of an acid.

V.—Tungstates.

Definition.—Salts formed from tungstic acid (H_2WO_4 or $\mathbf{W}O_2Ho_2$).

Tungstic acid forms both normal and acid salts. Many of the tungstates are of very complex constitution. They all redden litmus, and

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are all decomposed by hydrochloric acid, a hydrate of tungstic acid being precipitated (H_2WO_4,H_2O).

Uses.—Sodic tungstate ($Na_2WO_4,2aq$) is used by the calico-printers as a mordant, and also for the purpose of rendering muslins uninflammable. Tungstate of baryta has been used as a paint, in the place of white lead.

VI.—Molybdates.

Definition. — Salts formed from molybdic acid (H_2MoO_4 or MoO_2Ho_2?) [N.B.—MoO_3 has been obtained, but no definite hydrate is known.]

Normal and acid molybdates have been prepared. The alkaline molybdates are soluble.

Ammonic molybdate is used in the laboratory for the purpose of precipitating phosphoric acid. The solution must be first acidulated with nitric acid, and afterwards boiled.

VII.—Tellurates.

Definition.—Salts formed from telluric acid (H_2TeO_4 or TeO_2Ho_2). The tellurates are unstable salts. They give a black precipitate with H_2S. When heated they evolve oxygen, a tellurite remaining.

Other Oxy-Sulpho Salts.

VIII.—Hyposulphites or Hydrosulphites.

Definition.—Salts formed from hypo- or hydro-sulphurous acid (H_2SO_2 or SHo_2). The acid $H_2S_2O_3$, or $SS''OHo_2$ (thiosulphuric acid), is often improperly called hyposulphurous acid.

The *hyposulphites* are prepared by the action of zinc on solutions of the acid-sulphites, the zinc merely removing an atom of oxygen from the sulphite ($NaHSO_3+Zn=ZnO+NaHSO_2$). The sodic hyposulphite or hydrosulphite ($NaHSO_2$) is soluble in water, rapidly absorbs oxygen from the air, becoming $NaHSO_3$, possesses marked bleaching powers, reduces salts of silver, of mercury and of other metals, and when warmed with an oxalic acid solution, becomes of a deep orange tint, H_2SO_2 being liberated. This orange color of the solution rapidly disappears, free sulphur being deposited.

IX.—Thiosulphates or Sulpho-Sulphates (sometimes called Hyposulphites).

Definition.— Salts formed from dithionous, thiosulphuric, or sulphosulphuric acid (often called hyposulphurous acid) ($H_2S_2O_3=SS''OHo_2$).

The thiosulphate or hyposulphite of soda, ($Na_2S_2O_3$), as it is called, and other thiosulphates may be prepared either (1) by digesting

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together sulphur and a sulphite ($Na_2SO_3+S=Na_2S_2O_3$), or (2) by passing SO_2 through a solution of a metallic sulphide.

Sodic hyposulphite ($Na_2S_2O_3$) is prepared commercially, by exposing either the refuse of alkali works (soda or tank waste), or the refuse lime of gasworks which contains calcic sulphide, to the air, whereby a calcic hyposulphite is obtained ($2CaS+2O_2=CaS_2O_3+CaO$). When a solution of this salt is precipitated with sodic carbonate, the soluble sodic hyposulphite is formed, and calcic carbonate is precipitated ($CaS_2O_3+Na_2CO_3=CaCO_3+Na_2S_2O_3$).

The thiosulphates are sometimes called sulpho-sulphates, from being regarded as sulphates where a sulphur atom has displaced an oxygen atom (*e. g.*, Na_2SO_4—Na_2SSO_3). The thiosulphates are all decomposed by heat and by acids, sulphurous acid being evolved ($S_2O_2=S+SO_2$). For this reason a metallic sulphide is often precipitated when a hyposulphide is added to an acid solution of a metal. Thus "*antimony vermilion*" (Sb_2S_3) is prepared commercially by acting on an acid solution of chloride of antimony, prepared by dissolving crude antimony ore (Sb_2S_3) in hydrochloric acid, with calcic hyposulphite prepared from alkali waste.

Uses.—*Sodic Hyposulphite*, or thiosulphate, is used for extracting argentic chloride from an ore. It is largely used in photography, the alkaline thiosulphates being solvents of the insoluble argentic salts, thereby forming the sweet-tasted argentic thiosulphate, which, with any excess of sodic hyposulphite forms $NaAgS_2O_3$.

$2AgCl$	+	$Na_2S_2O_3$	=	$2NaCl$	+	$Ag_2S_2O_3$.
Argentic chloride	+	Sodic thiosulphate	=	Sodic chloride	+	Argentic thiosulphate.

[Note: The white AgCl, *i.e.*, the salt when unacted upon by light, is *entirely* soluble in $Na_2S_2O_3$. When the AgCl has been exposed to light it blackens, forming argentic subchloride, Ag_2Cl, and free chlorine. When this argentic subchloride (Ag_2Cl) is acted on with a solution of a hyposulphite, it is decomposed into $AgCl+Ag$, the chloride being soluble in the hyposulphite, the reduced metal remaining undissolved.

Sodic thiosulphate is also used as an "*antichlor*" for removing the last traces of chlorine from bleached goods, a process known as "*killing the bleach.*" It is also used in medicine (hyposulphite of soda, B.P.).

Tests.—(1.) Soluble thiosulphates dissolve the insoluble argentic salts.

(2.) *Lead salts;* white ppt. of plumbic thiosulphate (PbS_2O_3).

(3.) *Mercurous nitrate;* black ppt. of mercurous sulphide (Hg_2S).

(4.) The thiosulphates decolorise an alcoholic solution of iodine.

(5.) A thiosulphate is decomposed by HCl, the thiosulphuric acid ($H_2S_2O_3$) set free being instantly decomposed ($2H_2S_2O_3=2H_2SO_4+S_2$).

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Sulphites (Closely allied to Carbonates).

Definition.—Salts formed from sulphurous acid (H_2SO_3 or $SOHo_2$). The acid forms both normal and acid salts (*e.g.*, Na_2SO_3, $KHSO_3$).

Preparation.—By acting with sulphurous acid on the oxides or on the carbonates of the metals, either in solution or in suspension in water.

Properties.—The sulphites are solid inodorous salts. The alkaline sulphites are very soluble in common water, the sulphites of barium, strontium and calcium being also soluble in water containing free SO_2; the remaining sulphites are insoluble.

When heated they are decomposed with the liberation of SO_2.

When treated with *sulphuric acid* or with *hydrochloric acid*, SO_2 is evolved; *nitric acid* changes the sulphites into sulphates.

The sulphites have a great affinity, especially when moist, for oxygen, attracting it from the air. They act, therefore, as powerful reducing agents, changing ferrous to ferric salts, arsenic to arsenious acid; reducing chromic acid, and precipitating gold, tellurium, etc., from solutions containing an excess of hydrochloric acid.

Tests.—(1.) A sulphite, when treated with hydrochloric acid, evolves SO_2. Sulphurous acid is known by its action on paper moistened with starch and iodic acid.

(2.) Add to a sulphite dissolved in a little water, a fragment of zinc and hydrochloric acid; H_2S (known by its blackening lead paper) will be evolved.

(3.) *Argentic nitrate;* a white ppt. of *argentic sulphite*, soluble in excess of the sulphite. When boiled, the metal is partially reduced, and sulphuric acid formed.

(4.) *Baric nitrate;* a white ppt. of *baric sulphite*, *soluble in* HCl. If a few drops of chlorine water be added to this solution, *baric sulphate* is formed, which is *insoluble in acids*.

Uses.—The sulphates are employed to check fermentation, and to prevent the growth of fungi. They are also used as "antichlors" to expel chlorine ($Na_2SO_3 + H_2O + Cl_2 = Na_2SO_4 + 2HCl$.)

Hyposulphates (Dithionates).

Definition.—Salts formed from hyposulphuric or dithionic acid $H_2S_2O_6$ or $\left\{\begin{matrix}SO_2Ho\\SO_2Ho\end{matrix}\right)$.

Preparation.—The dithionate of manganese is prepared by passing SO_2 through ice-cold water containing peroxide of manganese ($MnO_2 + 2SO_2 = MnS_2O_6$).

Properties.—All the hyposulphates are soluble in water. They are all decomposed by heat, a sulphate being formed and SO_2 evolved. They are all decomposed when heated with sulphuric acid (SO_2 being given off), but they are unaffected by the cold acid, thereby distinguishing them from either sulphites or hyposulphites.

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The *trithionates* (salts of $H_2S_3O_6$); *tetrathionates* (salts of $H_2S_4O_6$), and *pentathionates* (salts of $H_2S_5O_6$) are unimportant.

N.B. *Action of Sulphuric Acid on Oxysulpho Salts.*

(α.) On *sulphates.* No odor is evolved, either with cold or hot, or with strong or dilute acid.

(β.) On *sulphites.* The odor of SO_2 is evolved with dilute acid in the cold.

(γ.) On *hyposulphates.* No odor is evolved with dilute acid in the cold, but SO_2 is evolved when the mixture is heated.

(δ.) On *thiosulphates.* The odor of SO_2 is evolved with a dilute acid, the action being accompanied with the deposition of sulphur.

Nitrates.

Definition.—Compounds formed from nitric acid(HNO_3 or NO_2Ho).

Synonyms.—*Azotates; Saltpetres.*

Natural History.—Nitrates are produced whenever the ammonia of organic matter is oxidized in the presence of an alkali. They are found in the shallow well-waters of towns as sewage products, formed by the oxidation of the nitrogen during the passage of animal matters through the soil. They are found, too, in the juices of plants, and in the urine of patients who have taken ammonia.

Potassic nitrate (KNO_3), or *prismatic nitre,* is found on the soil in India, the crude nitre extracted by solution and crystallization being imported into this country under the name of "grough." *Sodic nitrate* ($NaNO_3$) or *cubical nitre,* is found beneath the soil in Chili and Peru. Although sodic nitrate is unsuited for gunpowder manufacture, owing to its hygroscopicity and low oxidizing power, it is easily converted into potassic nitrate by the action of potassic chloride, a salt imported into this country from the salt mines of Stassfurth, as well as obtained from the refuse of the sugar beet manufacture ($NaNO_3+KCl=KNO_3+NaCl$).

Nitre heaps or plantations consist of masses of animal refuse mixed with old mortar, etc., and moistened from time to time with urine or stable runnings. These heaps are freely exposed to the air, but sheltered from the rain. In time nitrates of the several bases present are formed, and collect both on the surface of the heap and in the superficial layer of earth (nitrified earth).

Theories of Nitrification.—Two theories have been advanced to account for these changes.

I. Schönbein believed that the formation of the nitrates was due to the union of atmospheric oxygen and nitrogen, the combination being favored by the presence of porous solids and of matters undergoing oxidation.

II. Most chemists, however, hold that the nitrogen of the ammonia evolved as the organic matter putrefies, becomes oxidized, the oxida-

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tion being promoted by the presence of lime and of porous materials.* *Putrefying nitrogenized matters, moisture,* and free access of air are, therefore, the *essential conditions* of nitrification, whilst the presence of a *basic substance,* such as lime, to fix the acid formed, and of *porous* materials to assist oxidation, are the conditions that specially favor the action.

Impurities of *saltpetres.*—(*a.*) Insoluble earthy and vegetable matters; (*β.*) potassic and sodic chlorides and sulphates; (*γ.*) calcic sulphate; (*δ.*) moisture. Potassic chloride is, moreover, a special impurity of the potassic nitrate, manufactured from sodic nitrate.

Purification of nitre (Refining).—A saturated solution of the impure salt in *boiling* water is first prepared. This, whilst boiling, is filtered, to remove the *insoluble impurities.* The boiling filtrate is then placed in troughs and kept constantly agitated, so that the crystals of potassic nitrate that form may be small (*saltpetre flour*). As the water cools the nitrate crystallizes out, it being four or five times more soluble in hot than in cold water; whilst the sodic and potassic chlorides do not crystallize out, inasmuch as they are almost as soluble in cold as they are in hot water. In this way the separation of the chlorides from the nitre is effected. The nitre is then washed with a little water, the mother liquor and the washings being afterwards evaporated to dryness, and the residues added to the "grough" or impure nitre.

Any coloring matter present is got rid of by animal charcoal. A pure nitre is known—

(1.) By its solution in water being clear and neutral to test-paper.

(2.) By the absence of insoluble matter.

(3.) By argentic nitrate giving no precipitate (proving the absence of chlorides).

(4.) By baric nitrate giving no precipitate (proving the absence of sulphuric acid).

(5.) By ammonic oxalate giving no precipitate (proving the absence of lime).

Preparation (artificial).—By the action of nitric acid on metals, or on their oxides or carbonates.

Properties.—The nitrates are all crystallizable solids, of various colors and shapes; some are *rhombohedric* ($NaNO_3$), some *doubly oblique* ($Bi3NO_3$), but most generally *right prismatic.* They have a saline taste, but no odor. Many are anhydrous, but they more generally contain six molecules of water.

Action of heat.—They are all decomposed by heat, and generally fuse before decomposing.

(*a.*) In some cases the metal is entirely reduced by heat, as *e. g.*, the nitrates of the noble metals.

* Mr. Warrington has lately suggested that nitrification is a process similar to the acetic fermentation, and may be induced in an ammonia solution preserved in the dark by the action of a mycoderm.

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(β.) In some cases nitric peroxide (N_2O_4) and oxygen are evolved, an oxide remaining ($Pb2NO_3$; $Cu2NO_3$).

(γ.) Ammonic nitrate (H_4N,NO_3) breaks up into nitrous oxide (N_2O) and water.

(δ.) The alkaline nitrates are first changed into nitrites, oxygen being evolved, the nitrite being afterwards decomposed with the evolution of nitrogen and oxygen, the oxide only remaining.

In the presence of an oxidizable body (such as carbon) the action of heat on the nitrates is very energetic. Thus they deflagrate when placed on red-hot charcoal. (It should be noted that the chlorates and allied salts act similarly.)

Nascent hydrogen decomposes them, forming ammonia.

Sulphuretted hydrogen decomposes the nitrates of those metals that have a strong affinity for sulphuric acid, such as Ba, Pb, etc.

Action of water.—The nitrates are nearly all soluble in water, except the basic nitrates, such as the green basic cupric nitrate ($Cu2NO_3,3CuH_2O_2$). Mercurous nitrate ($Hg_2NO_3,2H_2O$) and bismuthous nitrate ($Bi3NO_3,5H_2O$) are decomposed by water, a basic salt being formed.

Many of the nitrates are deliquescent, such as $NaNO_3$, $Ca2NO_3$, NH_4NO_3, etc.

Action of acids.—The nitrates are all decomposed by acids. With *sulphuric acid* nitric acid is set free, and with *hydrochloric acid* chlorine. *The fixed acids* (such as phosphoric, boracic, etc.) decompose them by heat.

Action of alcohol.—They are generally insoluble in alcohol, excepting a few, such as calcic nitrate, cupric nitrate, strontic nitrate, etc.

Tests.—(1.) Hydrochloric acid, mixed with a nitrate, dissolves gold-leaf. (N.B.—A similar result occurs when HCl is added to solutions of chlorates, bromates, and iodates.)

(2.) If a nitrate be heated with a few drops of water, and a little sulphuric acid and a few copper turnings added, N_2O_2 will be evolved, which is known by its forming red fumes (N_2O_4) in the presence of air or oxygen. (When the nitrate is present in very small quantity, the presence of N_2O_4 may be known by its action on paper moistened with starch and potassic iodide.)

(3.) If a crystal of ferrous sulphate ($FeSO_4$) be dissolved in a nitrate solution, and sulphuric acid be poured down the sides of the test-tube so that it may form a layer at the bottom, a brown line will be produced at the junction of the two layers, due to the solution in one portion of the ferrous salt, of the nitric oxide set free by the deoxidizing power of another portion.

(4.) The conversion of the nitrogen of a nitrate into ammonia, by the action of nascent hydrogen set free either by zinc and sulphuric acid, or by a caustic soda solution and aluminium, and the estimation

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of the ammonia by Nesslerising, constitute a very delicate quantitative test for the presence and estimation of nitrates.

Uses.—For gunpowder, manures, and for the manufacture of nitric acid. The nitrates are in constant requisition in the laboratory as oxidizing agents.

In *medicine*, the ammonic, ferric, plumbic, argentic, and potassic nitrates, and a subnitrate of bismuth (really an oxy-nitrate, $BiONO_3$) are officinal.

OTHER NITRO-OXYGEN SALTS.

Nitrites.

Definition.—Compounds formed from nitrous acid (HNO_2 or NOHo).

Preparation.—(1.) By the action of nitrous acid on metallic oxides or hydrates ($KHO + HNO_2 = KNO_2 + H_2O$).

(2.) By the action of heat on certain nitrates, whereby oxygen is evolved ($KNO_3 = KNO_2 + O$).

(3.) By the oxidation of ammonia or nitrogenized organic matter (as in polluted well-water).

(4.) Nitrites of the alkalies, etc., may be prepared from nitrates, by stirring their boiling solutions with a rod of zinc or cadmium (Schönbein).

(5.) Ammonic nitrite is said to be produced during the spontaneous oxidation of phosphorus in the atmosphere, due to the action of ozone on moist air.

Properties.—The nitrites are soluble in water and in alcohol, in which latter solvent, for the most part, the nitrates are insoluble. The nitrites of silver, sodium and lead are anhydrous. Several double nitrites have been prepared, as *e.g.*, a compound of nitrite of potassium with a nitrite of either barium, zinc, or nickel.

Acid solutions of the nitrites act both as (α) *oxidizing* agents, as shown by their decolorizing indigo, and also (β), as *reducing* agents, as shown by their decolorizing potassic permanganate, reducing potassic chromate to a green chromium salt, and auric chloride or a mercurous salt to their respective metals.

Tests.—(1.) *Argentic Nitrate.* A white ppt. of argentic nitrite ($AgNO_2$).

(2.) A nitrite solution, acidulated with *a few drops* of sulphuric acid, sets free iodine from KI, which turns blue with starch. (This test gives no action with nitrates.)

[Note: If organic matter be present in the solution, the nitric acid set free from a nitrate by sulphuric acid, may be reduced, and will then show the reactions of a nitrite. Hence, in such a case, acetic acid should be added, the liquid distilled, and the distillate tested.]

Uses.—Nitrite of ethyl ($C_2H_5NO_2$) is the chief constituent of spiritus ætheris nitrosi (sweet spirit of nitre).

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The Hyponitrites (salts of N_2O as NaNO) are of no importance. Sodic hyponitrite (NaNO) is said to be formed by the action of sodium amalgam on a nitrate. On the addition of an acid N_2O is evolved.

Salts Allied to the Nitrates.

Chlorates (formed from *chloric acid*, $HClO_3$, or $\left\{\begin{matrix}OCl\\OHo\end{matrix}\right.$); *Bromates* (formed from *bromic acid*, $HBrO_3$, or $\left\{\begin{matrix}OBr\\OHo\end{matrix}\right.$); *Iodates* (formed from *iodic acid*, HIO_3 or $\left\{\begin{matrix}OI\\OHo\end{matrix}\right.$).

We shall consider these together.

Natural History.—None of them are found native.

Preparation.—By the action of chlorine, bromine, or iodine on a metallic hydrate. Thus—

$$\underset{\text{Potassic hydrate}}{6KHO} + \underset{\text{Chlorine}}{3Cl_2} = \underset{\text{Potassic chloride}}{5KCl} + \underset{\text{Potassic chlorate}}{KClO_3} + \underset{\text{Water.}}{3H_2O}.$$

$$6OKH + 3Cl_2 = 5KCl + \left\{\begin{matrix}OCl\\OKo\end{matrix}\right. + 3OH_2$$

Properties.—They are all very nearly related to nitrates. In one respect the *iodates* are peculiar, viz., that a basic molecule may combine with more than one molecule of the acid. Thus we have—(1.) *Normal potassic iodate* (KIO_3); (2.) *Potassic diiodate* ($2KIO_3,I_2O_5$); (3.) *Potassic triiodate* (KIO_3,I_2O_5).

Action of Heat.—The chlorates, bromates, and iodates are all decomposed by heat, one of two results occurring—either (α.) Oxygen only is driven off—a *chloride*, *bromide*, or *iodide* remaining—*i.e.*, if the affinity of the metal for the haloid is greater than it is for oxygen. Thus $2KIO_3=2KI+3O_2$; or, conversely—

(β.) Oxygen and the haloid element are both given off, an *oxide* remaining, *i.e.*, if the affinity of the metal for oxygen is greater than it is for the haloid. Thus $2(Ba2IO_3)=2BaO+5O_2+2I_2$.

Mixed with a combustible element they all deflagrate when heated, and explode when struck. Paper soaked in their solutions and dried burns like touch-paper.

Action of acids.—They are all decomposed by acids. *Sulphuric acid* decomposes them, setting free from the chlorates the yellow chloric peroxide (Cl_2O_4), whilst from the bromates and iodates, oxygen and bromine, or oxygen and iodine, are set free respectively. *Hydrochloric acid* liberates euchlorine from the chlorates, and chlorine with bromine, or chlorine with iodine, from the bromates and iodates respectively. *Nitric acid* forms with the chlorates a nitrate and a perchlorate, with the liberation of oxygen and chlorine.

Action of water.—The *chlorates* are nearly all soluble in water, and are deliquescent (mercurous chlorate excepted). The *bromates* are mostly soluble in water, the mercurous, silver and lead bromates being

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the least soluble. The *iodates*, excepting the alkaline iodates, are but sparingly soluble in water.

Action of alcohol.—Many of the salts are soluble in alcohol.

All the salts of this group act as oxidizing agents. The chlorates for this purpose are in constant use in the laboratory, chloric acid being set free by the action of hydrochloric acid upon them. In this way protosalts may be changed to persalts.

Tests.—They all deflagrate when placed on red hot charcoal.

Chlorates.—(1.) No precipitate with *argentic nitrate;* a chlorate is thus known from a chloride. If the salt be one (like $KClO_3$) forming a chloride by heat, the solution of the residue after ignition (KCl) will give a precipitate of AgCl with argentic nitrate.

(2.) Add a few drops of indigo to a solution of a chlorate. On adding a solution of sulphurous acid, the indigo will be bleached. A chlorate may in this way be known from a nitrate, for with the latter the blue color remains unaltered.

(3.) On heating a chlorate with HCl the yellowish green gas called *euchlorine* is evolved.

(4.) On adding sulphuric acid to a chlorate, *chloric peroxide* is evolved.

Bromates.—Bromine is set free when a bromide is heated with sulphuric acid.

Iodates.—If a sulphurous acid solution be added to a solution of an iodate, an iodide is formed ($KIO_3 + 3H_2SO_3 = KI + 3H_2SO_4$). The iodide may then be detected in the usual way, with $AgNO_3$ or by starch.

OTHER OXY-SALTS OF CHLORINE, BROMINE, AND IODINE.

Perchlorates and Periodates.

Definition.—Salts formed from *perchloric acid* $\left(HClO_4 \text{ or } \begin{cases} OCl \\ O \\ OHo \end{cases}\right)$ and from *periodic acid* $\left(HIO_4 \text{ or } \begin{cases} OI \\ O \\ OHo \end{cases}\right)$.

Potassic perchlorate is formed either by heating potassic chlorate, discontinuing the heat when one-third of the oxygen has been evolved ($2KClO_3 = KCl + KClO_4 + O_2$); or by acting on potassic chlorate with boiling nitric acid ($3KClO_3 + 2HNO_3 = 2KNO_3 + H_2O + KClO_4 + Cl_2 + 2O_2$).

Sodic periodate is formed by the action of chlorine on a mixed solution of sodic hydrate and iodate ($NaIO_2 + 2NaHO + Cl_2 = NaIO_4 + H_2O + 2NaCl$).

The *perchlorates* are all soluble in water, and many are soluble in alcohol. They are all decomposed by heat, with the formation of a chloride and the evolution of oxygen.

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The *periodates* are sparingly soluble in water, but soluble in dilute nitric acid. They are all decomposed by heat. Periodic acid has a tendency to form *basic* salts, just as iodic acid has a tendency to form *acid* salts.

To distinguish a chlorate from a perchlorate, add a few drops of sulphuric acid to some crystals of the salt. A yellow gas is evolved in the case of chlorates, but none in the case of perchlorates.

Chlorites.

Definition.—Salts formed from chlorous acid ($HClO_2$ or **O**ClHo).

Preparation.—By the action of chlorous acid upon a base.

Properties.—The chlorites are solid deliquescent salts, decomposed by heat and by the feeblest acids (as CO_2). They possess considerable bleaching power, and deoxidize an acidulated solution of potassic permanganate.

Hypochlorites.

Definition.—Salts formed from hypochlorous acid (HClO or **O**ClH or ClHo).

Preparation.—By the action of hypochlorous acid on metallic oxides or hydrates.

KHO	+	HClO	=	KClO	+	H_2O.
Potassic hydrate	+	Hypochlorous acid	=	Potassic hypochlorite	+	Water.
(**O**KH	+	Cl**H**o	=	ClKo	+	**O**H_2).

Properties.—The hypochlorites are bleaching salts, and are decomposed by the feeblest acids. Heat decomposes them, forming a chloride and a chlorate ($3KClO = 2KCl + KClO_3$).

The interest of the hypochlorites is centred in what is called "*chloride of lime*," or bleaching powder. This is prepared by acting on slaked lime (calcic hydrate) with chlorine. The temperature must be maintained below 100° F., or otherwise calcic chloride and chlorate would be formed. The potassic and sodic chlorides are prepared in a similar manner. It was formerly thought that a *chloride* and a *hypochlorite* were formed during this process. Thus—

$2CaH_2O_2$	+	$2Cl_2$	=	$CaCl_2$	+	$Ca''Cl_2O_2$	+	$2H_2O$.
Calcic hydrate	+	Chlorine	=	Calcic chloride	+	Calcic hypochlorite	+	Water.
(2**Ca**Ho_2	+	$2Cl_2$	=	**Ca**Cl_2	+	$Cao''Cl_2$	+	2**O**H_2).

but of this there is considerable doubt, inasmuch as bleaching-powder contains no calcic chloride, and is not deliquescent (when properly made). Hence the composition of bleaching-powder is usually stated as consisting of a calcic chloride hypochlorite, CaCl(OCl). Thus—

CaH_2O_2	+	Cl_2	=	CaCl(OCl)	+	H_2O.
Calcic hydrate	+	Chlorine	=	Bleaching powder	+	Water.
(**Ca**Ho_2	+	Cl_2	=	**Ca**(OCl)Cl	+	**O**H_2).

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When "*chloride of lime*" is exposed to the air it gives off chlorine, by the action of atmospheric carbonic anhydride upon it. Hence its use *as a disinfectant.* The evolution of chlorine is considerable when a strong acid is added to the compound ($Ca(OCl)Cl + H_2SO_4 = CaSO_4 + H_2O + Cl_2$). It is also used *as a bleaching agent* (depending on the oxidizing action of chlorine), the goods being first digested in a solution of bleaching-powder, and afterwards transferred to a weak acid solution, whereby the chlorine is set free and the bleaching effected.

To distinguish a chlorite from a hypochlorite, add to the solution of the salt a solution of arsenious anhydride and nitric acid; the bleaching power of the *chlorites* remains unaffected, whilst that of the *hypochlorites* is destroyed.

Phosphates (*see* page 134).

Classification:—

Orthophosphates, compounds formed from orthophosphoric acid, H_3PO_4.
Pyrophosphates, ,, ,, pyrophosphoric acid, $H_4P_2O_7$.
Metaphosphates, ,, ,, metaphosphoric acid, HPO_3.

I.—Orthophosphates, or *Common Phosphates.*

Definition.—Salts of tribasic phosphoric acid, H_3PO_4, or $POHo_3$.

Preparation of *Hydric Disodic Phosphate* (common sodic phosphate).—By the action of sodic carbonate on acid calcic phosphate.

Varieties of Orthophosphates.—One or all of the hydrogens of the acid may be replaced by a metal. Thus—

NaH_2PO_4=Sodic-dihydrogen phosphate (superphosphate). } *Acid salts.*
Na_2HPO_4=Disodic-hydrogen phosphate }
Na_3PO_4 =Trisodic phosphate ... ... *Normal salt.*

Or the three hydrogens may be replaced by different metals. Thus—$HNaNH_4PO_4 + 4aq$=Hydric sodic ammonic phosphate (*microcosmic salt*).

Properties.—The orthophosphates are solid salts, having a saline taste but no odor. They fuse by heat, but are not decomposed if the base of the salt be a fixed one. Acids decompose and dissolve them. The phosphates of the alkalies are soluble in water, but the rest are insoluble. The insoluble phosphates, excepting calcic phosphate, are decomposed on boiling with sodic carbonate.

Tests.—(1.) *Argentic nitrate;* a yellow ppt. in a neutral solution (Ag_3PO_4).

(2.) *Magnesic sulphate and ammonia;* a white ppt. ($NH_4MgPO_4 + 6H_2O$), which by heat becomes $Mg_2P_2O_7$ (100 parts=63·96 of P_2O_5).

(3.) *Ammonic molybdate;* a yellow ppt. when boiled in a solution containing HNO_3.

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II.—Pyrophosphates.

Definition.—Salts of pyrophosphoric acid ($H_4P_2O_7$, or $P_2O_3Ho_4$).

Preparation of *Sodic pyrophosphate.*—By igniting common sodic phosphate. (Thus, $2Na_2HPO_4=H_2O+Na_4P_2O_7$.)

Most of the pyrophosphates are solid, excepting the salts of potassium and ammonium. They are easily converted into meta- and ortho-phosphates, by the addition or abstraction of water, or of a metallic base.

Tests. — *Argentic nitrate;* a white ppt. in alkaline solutions ($Ag_4P_2O_7$).

III.—Metaphosphates.

Definition.—Salts of metaphosphoric acid (HPO_3, or PO_2Ho).

Preparation of *Sodic metaphosphate.*—By the ignition of microcosmic salt ($HNaNH_4PO_4=NaPO_3+NH_3+H_2O$).

Test.—*Argentic nitrate;* a white gelatinous ppt. ($AgPO_3$).

Two other phosphates have been studied by Fleitmann and Henneberg. They are formed by fusing together, (1) one part of pyrophosphate and two of metaphosphate, the salt formed having the composition $2Na_3PO_4,P_2O_5$; and (2) one part of pyrophosphate and eight of metaphosphate, the salt formed having the composition $4Na_3PO_4,3P_2O_5$. They are unstable salts, but form definite argentic and magnesic compounds (*see* page 139).

All phosphates are converted into tribasic phosphates by fusion with an alkaline hydrate or carbonate.

Other Oxy-Phosphorus Salts.

Hypophosphites.

Definition.—Salts formed from hypophosphorous acid (HPH_2O_2, or POH_2Ho).

Preparation.—By acting on a metallic hydrate with phosphorus ($P_8+6H_2O+3CaH_2O_2=3(Ca''2PH_2O_2)+2PH_3$.

Properties.—The salts are monobasic, as, *e.g.*, $NaPH_2O_2$ and $Pb''2PH_2O_2$. They are all deliquescent crystalline stable solids. By evaporating down their solutions they are converted into phosphites. The hypophosphites reduce gold and silver salts. They are all soluble in water; whilst the alkaline hypophosphites are also soluble in alcohol. They are all decomposed by heat.

"*Sodæ hypophosphis*" is a pharmacopœial preparation.

Phosphites.

Definition.—Salts formed from phosphorous acid (H_2PHO_3, or $POHHo_2$).

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These salts may be *normal* (M_2PHO_3), or *acid* ($MHPHO_3$).

Properties. — Solid bodies, sparingly soluble in water, except the phosphates of the alkalies, which are freely soluble. On the application of heat, the *normal* phosphites evolve hydrogen and phosphoretted hydrogen, whilst the *acid* phosphites evolve hydrogen only, and leave a metaphosphate.

Tests.—(1.) *Mercuric chloride;* a white ppt. of calomel in a solution acidulated with acetic acid.

(2.) *Sulphurous acid* is reduced by the phosphites to H_2S, the precipitation of sulphur resulting from the action of the H_2S on the excess of sulphurous acid ($3H_2PHO_3+H_2SO_3=3H_3PO_4+H_2S$).

ALLIES OF THE PHOSPHATES.

Arsenates (salts of arsenic acid, H_3AsO_4, or $AsOHo_3$); *Antimonates* (salts of antimonic acid, or antimonic anhydride Sb_2O_5).

Arsenates.

Definition.—Salts formed from arsenic acid (H_3AsO_4 or $AsOHo_3$).

The arsenates are isomorphous with the phosphates. Thus—

$Na_3AsO_4,12H_2O$ is prepared by adding an excess of sodic hydrate to arsenic acid, and evaporating.

$Na_2HAsO_4,12H_2O$ is prepared by adding sodic carbonate to a hot solution of arsenic acid until effervescence ceases, and evaporating.

NaH_2AsO_4,H_2O is prepared by adding to the previous salt an equivalent quantity of arsenic acid to that which it already contains.

KH_2AsO_4 is prepared by fusing together nitre and arsenious acid, dissolving the residue in water, and crystallizing.

$(H_4N)MgAsO_46H_2O$, a body isomorphous with the phosphate salt, is prepared by adding magnesic sulphate to a solution of an alkaline arsenate to which ammonia has been added.

Properties.—In form and reactions the arsenates are very similar to the tribasic phosphates. Arsenates are also known corresponding to the meta- and pyro-phosphates ($Na_4As_2O_7$). The arsenates may be prepared in an anhydrous state, but when redissolved they recover their basic water. Heat alone, provided a fixed base be present, does not decompose them. They are decomposed by nascent hydrogen, arseniuretted hydrogen being evolved. Acids decompose them. Water dissolves the alkaline arsenates only, but they are all soluble in dilute nitric acid.

Tests.—(1.) *Lime, lead,* and *barium salts;* white ppts.

(2.) *Argentic nitrate;* a brownish-red ppt. of triargentic arsenate (Ag_3AsO_4). (This test distinguishes the arsen*ates* from the arsen*ites*.)

(3.) *Sulphuretted hydrogen;* a yellow ppt. of As_2S_5, soluble in ammonia.

(4.) Add a few drops of *cupric sulphate,* and carefully drop in *dilute*

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ammonia until a green precipitate is produced ($CuHAsO_4$). *The arsenate solution must be neutral.* The cupric arsenate is soluble in acids and in alkalies.

Uses.—The arsenate of soda and the arsenate of iron (Fe_32AsO_4) are used in *medicine.*

The **Vanadates,** or salts of a base and vanadic anhydride (V_2O_5), have been studied by Roscoe. They are usually red or yellow bodies. Boiled with sulphuric acid, alcohol, and sugar, or heated with sulphuretted hydrogen or sulphurous acid, they form a deep blue solution.

The **Antimonates** closely resemble the arsenates. The alkaline salts are obtained by the action of antimonic anhydride on a hydrate. They are decomposed by an acid, $Sb_2O_54H_2O$ being precipitated. There are said to be two modifications of antimonic acid, viz., *antimonic acid,* forming the normal salts $K_2Sb_2O_6$, and *metantimonic acid,* which forms the normal salt $K_4Sb_2O_7$.

The *soluble acid metantimonate of potassium* ($K_2H_2Sb_2O_7,6H_2O$) precipitates soda-salts as an insoluble acid sodic metantimonate ($Na_2H_2Sb_2O_7,6H_2O$). The acid potassic salt rapidly changes to a normal salt, but this latter does not effect the precipitation of sodic compounds.

Other Oxy-Arsenicum Salts.

The **Arsenites** of the alkalies may be formed by dissolving arsenious anhydride (As_2O_3) in solutions either of the alkalies or of the alkaline carbonates. M'_3AsO_3 is believed to represent the formula for these salts. The alkaline arsenites are soluble in water; the arsenites of the earths are insoluble in water, but are soluble in acids.

The *tripotassic arsenite* (Fowler's solution, or liquor arsenicalis) (K_3AsO_3), is used in medicine. The alkaline arsenites are used as sheep-dipping mixtures, and also by naturalists as an arsenical soap to preserve the skins of animals. Sodic arsenite is used to prevent the incrustation in boilers.

Cupric arsenite, or "*Scheele's green,*" ($CuHAsO_3$), and a mixed *cupric arsenite and acetate,* or "*Schweinfurt green*" ($3CuAs_2O_4,Cu2C_2H_3O_2$), are used as pigments.

The arsenites have a great tendency to become arsenates, owing to the greater stability of the latter.

Carbonates.

Definition.—Salts formed from carbonic acid (H_2CO_3 or CO_2Ho_2 (?)).

Natural History.—They are found in all three kingdoms of nature; (α.) in the *mineral* kingdom (as *e. g.,* $CaCO_3$, etc.); (β.) in the

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vegetable, as *e. g.*, pearlash (potassic carbonate) in the ashes of land-plants, and sodic carbonate in the ashes of marine plants; (γ.) in the *animal* kingdom, carbonates are found in bones, shells, blood, urine, deposits, etc.

Preparation.—(1.) Sodic carbonate is prepared from sodic chloride, by first converting it into a sulphate, and afterwards heating it with chalk and coal (see page 302).

(2.) From the ashes of plants by lixiviating.

(3.) By the action of an alkaline carbonate on a metallic salt ($Pb_2NO_3 + Na_2CO_3 = 2NaNO_3 + PbCO_3$).

[N.B.—The carbonates are never formed by the action of carbonic anhydride on a dry metallic oxide.]

Properties.—The carbonates generally crystallize in right prisms; some in oblique prisms (Na), and some in rhomboids (Ca, Fe, Zn).

Action of heat.—Ammonic carbonate volatilizes when heated. The carbonates of the alkaline metals and barium are unaffected by heat. All other carbonates are decomposed, CO_2 being evolved, and a metallic oxide left.

Action of acids.—All carbonates are decomposed by acids, with the evolution of CO_2.

Action of water.—The alkaline carbonates are soluble in water. Many carbonates that are insoluble in common water, are soluble in water containing CO_2 in solution, but are deposited as the CO_2 escapes. Many of them are anhydrous.

Tests.—An acid sets free CO_2, which whitens baryta or lime-water (forming $BaCO_3$ and $CaCO_3$), the precipitates being soluble in an acid.

Uses.—The sodic salt is largely used in every day life, and also in medicine. The ammonic, bismuthic (really an oxycarbonate), ferrous (which mixed with sugar forms the saccharated carbonate), lithic, magnesic, potassic, and zincic carbonates are also used medicinally.

Silicates.

Definition.—Compounds of silicic acid [viz., H_4SiO_4 or $SiHo_4$ (*tetrabasic acid*); and also of H_2SiO_3 or $SiOHo_2$ (*dibasic acid*), this latter acid being said to be produced by the evaporation "in vacuo" of a solution of the tetrabasic acid].

Natural History.—They are found in nature abundantly, as clay, felspar, mica, etc.

Varieties.—The salts having the formula M'_4SiO_4, have been named *ortho-silicates*, and the salts with the formula M'_2SiO_3 *meta-silicates*. There exists also an intermediate class, formed by the combination of a molecule of each. The double silicates are numberless.

Preparation of Alkaline Silicates.—By fusing silicic anhydride or the insoluble silicates, with the alkaline hydrates or carbonates.

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Properties.—*Action of heat.* The silicates are mostly fusible, their fusibility being increased by admixture.

Action of water.—They are all insoluble in water, excepting the alkaline silicates which contain an excess of base.

Action of acids.—The anhydrous, normal and acid silicates of the earths, are not decomposed by any acid except hydrofluoric. The hydrated silicates are decomposed by all acids. If CO_2 be passed through a solution of sodic silicate, silicic acid is precipitated as a gelatinous deposit.

The silicates are alkaline to turmeric.

The **Borates** (salts of boracic or boric acid BHo_3 or HBO_2,H_2O), are formed by the action of the acid on metallic hydrates, oxides or carbonates. They resemble the silicates in the variety of the proportions in which they enter into combination with the alkaline bases. All the borates are more or less soluble in water, the alkaline borates being very soluble and the others less so. They are all soluble in dilute nitric acid. The borates impart a green light to flame.

Double Salts.

Definition.—Salts in which the displaceable hydrogens of the acid have been exchanged by different metals, or compound radicals.

Varieties.—(I.) *Salts formed by a combination of two metals with the same acid radical.*

(α.) The bicarbonates ($HNaCO_3$), binoxalates, etc., are thus double salts, the hydrogen playing the part of a metal.

(β.) One hydrogen of a dibasic acid may be displaced by one metal, and the second hydrogen by a different metal, as in Rochelle salt, where sodium and potassium are combined with tartaric acid ($KNaC_4H_4O_6$), or as in the sodic potassic disulphate (NaK_32SO_4), where $2SO_4$ is combined with K_3 and Na.

Thus we have double sulphates, double carbonates, double silicates, etc.

(II.) *Combinations of oxides of different classes with their several equivalents of the acid radical.*

Thus in common alum we have a sulphate of potash combined with a sulphate of alumina or K_2O,SO_3 with $Al_2O_3,3SO_3$, forming the compound $K_2Al_24SO_4+24aq$.

(III.) *Combinations of salts with saline or constitutional water.*

Thus one molecule of water in magnesic sulphate ($MgSO_4,H_2O+6H_2O$) cannot be expelled by a heat of 212° F., as the other six molecules of water may be. This seventh H_2O, represents a salt (and is hence called saline water), and may be replaced in the salt by a molecule of certain anhydrous salts not isomorphous with it, such as potassic sulphate, forming ($MgSO_4K_2SO_46H_2O$).

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IV. *The combinations of two acid radicals to one basic radical.* These are comparatively unimportant, and can scarcely be regarded as true double salts.

V. *The combinations of haloid salts with haloid salts,* as *e. g.,* the potassic platinic chloride ($2KClPtCl_4$).

Preparation.—Double salts are prepared (1) either by mixing together solutions of two salts in equivalent proportions, or (2) by the fusion of the two salts.

The following are some of the double salts :—

1. **Double Haloid Salts.**—*Where an alkaline haloid salt is combined with a haloid salt of a metal, having a feebler affinity for oxygen than the alkaline salt,* as ($KClPtCl_4$) ($NaCl,AuCl_32H_2O$).

2. **Double Sulphur Salts.**—(α.) *Double sulphides,* as *e. g.,* alkaline sulphides with higher sulphides ($3Na_2S,As_2S_5,15H_2O$); ($3Na_2S,Sb_2S_5$, $18H_2O$). (β.) *Hydrosulphides,* as *e.g.,* (KHS); (MgH_2S_2). (In these salts H acts as a metal).

3. **Double Oxysalts.**—(α.) *Double sulphates,* such as the *acid sulphates* or *bisulphates* ($NaHSO_4$); the *alums*; and such other double sulphates as N_2Ca2SO_4 (*glauberite*), $MgSo_4,K_2SO_46H_2O$; and also soda with magnesia, potash with manganese or with zinc, etc.

(β.) *Double carbonates,* such as $MgCa2CO_3$ (*dolomite*), $BaCa2CO_3$ (*baryto-calcite*), etc.

(γ.) *Double silicates,* such as alumina with potash (*felspar*), with soda (*albite*), with lime (*anorthite*), with glucinum (*emerald*), etc. *Porcelain* is a double silicate of lime and alumina, *glass* of potash or soda with lime, magnesia, alumina, lead, etc.

(δ.) *Double tartrates,* such as Rochelle salt. Similarly there are *double citrates,* etc.

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CHAPTER XII.

THE ALKALINE METALS.

	Symbol.	Atomic Weight.	Atomic Volume.	Specific Heat.	Fusing Point. °C.	Fusing Point. °F.	Specific Gravity.	Electric Conductivity 68—71F.
Potassium	K	39·1	45·20	0·16956	62·5	144·5	0·865	20·85
Sodium	Na	23·0	23·66	0·29340	97·6	207·7	0·972	37·43
Lithium	L	7·0	11.80	0·94080	180·0	356·0	0·593	19·0
Cæsium	Cs	133·0	(?)	(?)	(?)	(?)	(?)	
Rubidium	Rb	85·4	56·18	..	38·5	101·3	1·52	
Ammonium..	NH_4 (or Am)	18·0		(?)	(?)	(?)	(?)	

General Remarks.

Characters.—The alkaline metals decompose water at ordinary temperatures, forming soluble oxides and carbonates, having an alkaline reaction.

History.—The existence of a metal in the alkalies was prophesied by Lavoisier (1793). Sir H. Davy obtained potassium and sodium in 1807, by decomposing the alkalies with the galvanic battery. Lithia was first prepared by Arfvedson in 1817, the existence of the metal lithum being afterwards demonstrated by Davy. It was first prepared in quantity by Matthiessen (1855). (Phar. Journ., XV., p. 231.) Rubidium and cæsium were discovered by Bunsen and Kirchhoff in 1860, by their peculiar spectra.

General Properties.—(α.) *Physical.* The alkaline metals are soft, easily fusible, and volatile.

(β.) *Chemical.* They tarnish rapidly in the air. They decompose water and liberate hydrogen at ordinary temperatures. They are univalent. They furnish several oxides, but only one basic oxide (M'_2O), this oxide being deliquescent, very caustic, and very alkaline to test paper. The hydrates (MHO) cannot be decomposed by heat. They rapidly absorb CO_2, forming both normal and acid carbonates. The alkaline metals form but one chloride. Nearly all their salts are soluble and alkaline.

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POTASSIUM (K_2).

Atomic weight, 39·1. *Atomicity Monad* (′) (KCl, KI). *Specific gravity*, 0·865. *Fuses at* 144·5° F. (62·5° C.). *Boils at a low red heat.*

History.—Discovered by Davy (1807).

Natural History.—Found (α.) in the animal kingdom; (β.) in the vegetable kingdom, as a sulphate, chloride, and also combined with vegetable acids; (γ.) in the mineral kingdom, in sea and spring water, and in such bodies as alum, felspar, mica, etc.

Preparation.—(1.) By decomposing potassic carbonate with charcoal (Curandau and Brunner), as follows:—

(α.) The crude tartar from wine casks (*i.e.* hydric potassic tartrate, $KHC_4H_4O_6$) is first incinerated, whereby a residue of potassic carbonate and carbon is formed—

$2KHC_4H_4O_6$	=	K_2CO_3	+	$5H_2O$	+	$4CO$	+	$3C$.
Hydric potassic tartrate	=	Potassic carbonate	+	Water	+	Carbonic oxide	+	Carbon.

(β.) This residue is now intensely heated, when the metal distils over and is received into naphtha—

K_2CO_3	+	C_2	=	$3CO$	+	K_2.
Potassic carbonate	+	Carbon	=	Carbonic oxide	+	Potassium.

(Chalk is commonly added to the mixture to prevent fusion.)

(2.) By the electrolysis of potassic hydrate (Davy, 1807), ($2KHO = \underset{-}{K_2} + \underset{+}{H_2 + O_2}$).

(3.) By the action of white hot iron on potassic hydrate (Gay Lussac, 1808), ($4KHO + 3Fe = Fe_3O_4 + 2K_2 + 2H_2$).

Properties.—(α.) *Physical.* Potassium is a soft silvery-white metal. It has a less specific gravity than water, and therefore floats upon it. It is brittle at 32° F. (0° C.), but becomes malleable at a little above this temperature. At a red heat it forms a green gas. Its spectrum consists of two red lines at A and B, and a violet line at the blue end.

(β.) *Chemical.* It oxidizes instantly in air, and burns with a violet flame when heated. It removes oxygen from CO_2 when heated in its presence, liberating carbon ($2K_2 + 3CO_2 = 2KCO_3 + C$). It decomposes water at ordinary temperatures, liberating hydrogen ($K_2 + 2H_2O = 2KHO + H_2$). It burns in chlorine. It decomposes H_2S, forming K_2S ($SH_2 + K_2 = K_2S + H_2$).

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Compounds of Potassium.

		Salts.	Formula (General).	Formula (Constitutional).	Molecular Weight.	Specific Gravity.	Contains K_2O or equal to K_2O per cent.
1	Oxides.	Potassic oxide (potash, potassa)	K_2O	OK_2	94·2		100·0
2		Potassic dioxide	K_2O_2	O_2K_2	110·2		85·48
3		,, peroxide	K_2O_4	OK O O OK	142·2		66·24
4		,, hydrate (caustic potash)	KHO	OKH	56·1	2·1	83·95
5		Potassic chloride	KCl	KCl	74·6	1·994	63·13
6		,, iodide	KI	KI	166·1	3·056	28·35
7		,, bromide	KBr	KBr	119·1	2·670	39·54
8		,, fluoride	KF	KF	58·1	2·454	81·06
9		,, hydric fluoride	KHF_2	KF,HF	78·1		
10		,, fluosilicate ..	$2KF,SiF_4$	$2KF,SiF_4$	220·7		42·68
11	Cyanides.	,, cyanide	KCy	KCN	65·1		72·30
12		,, ferrocyanide (yellow prussiate) ..	K_4Cy_6Fe	$K_4Fe(CN)_6$	368·4		51·14
13		Potassic ferricyanide (red prussiate)	K_3Cy_6Fe	$K_3Fe(CN)_6$	329·3		42·90
14	Sulphides.	Dipotassic sulphide (protosulphide)	K_2S	SK_2	110·2		85·48
15		Dipotassic disulphide ..	K_2S_2	K_2S_2	142·2		
16		,, trisulphide (sesquisulphide) ..	K_2S_3	K_2S_3	174·2		
17		Dipotassic tetrasulphide	K_2S_4	K_2S_4	206·2		
18		,, pentasulphide (persulphide)	K_2S_5	K_2S_5	238·2		
19		Potassic sulph-hydrate (hydric sulphide) ..	KHS	KHs	72·1		
20	Sulphates.	Dipotassic sulphate (normal salt)	K_2SO_4	SO_2Ko_2	174·2	2·66	K_2O 54·07
21		Hydric potassic sulphate (acid salt)	$HKSO_4$	SO_2HoKo	136·1	2·475	
22	Carbonates.	Dipotassic carbonate(normal salt)	K_2CO_3	$COKo_2$	138·2	2·267	K_2O 68·17
23		Hydric potassic carbonate (acid salt)	$HKCO_3$	COHoKo	100·1	2·052	
24		Potassic nitrate (nitre or saltpetre)	KNO_3	NO_2KO	101·1	2·070	46·59
25		Potassic nitrite	KNO_2	NOKo	85·1		
26	Chlorates.	,, chlorate	$KClO_3$	OCl OKo	122·6	2·326	38·42
27		,, perchlorate ..	$KClO_4$	OCl O OKo	138·6		33·98
28	Tartrates.	,, tartrate	$K_2C_4H_4O_6$		226·2		
29		Hydric potassic tartrate (cream of tartar) ..	$KHC_4H_4O_6$		188·1		
30		Sodic potassic tartrate (Rochelle salt)	$KNaC_4H_4O_6$		210·1		
31		Potassic antimonious tartrate (tartar emetic) ..	$K(SbO_2)C_4H_4O_6$	$CO(SbO_2)$ CHHo CHHo COKo	341·1		
32		Potassic silicate (water glass)	SiK_4O_4	$SiKo_4$			

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COMPOUNDS OF POTASSIUM AND OXYGEN AND HYDROXYL.

Potassic oxide	...	...	...	K_2O.
Potassic dioxide	...	...	...	K_2O_2.
Potassic peroxide	...	...	...	K_2O_4.
Potassic hydrate	...	...	...	KHO.

(1.) Potassic Oxide; *Potassa; Anhydrous potash* (K_2O).

Preparation.—(1.) By heating together potassium and potassic hydrate ($2KHO + K_2 = 2K_2O + H_2$).

(2.) By fusing a mixture of potassium and potassic peroxide in an atmosphere of nitrogen ($K_2O_4 + 3K_2 = 4K_2O$).

Properties.—A white, deliquescent solid, possessing powerful basic properties. It combines with water with the evolution of great heat and the formation of potassic hydrate ($K_2O + H_2O = 2KHO$). It fuses at a red heat, and volatilizes at high temperatures.

(2.) Potassic Dioxide (K_2O_2), and **(3.) Potassic Peroxide** (K_2O_4) do not form corresponding salts with acids.

(4.) Potassic Hydrate; *Potash; Caustic potash* (KHO, or OKH, or KHo).

Preparation.—(1.) By the action of calcic hydrate (CaH_2O_2) on a dilute solution of potassic carbonate (*pearlash*) ($K_2CO_3 + CaH_2O_2 = 2KHO + CaCO_3$). The solution of potassic hydrate (KHO) must be decanted from the insoluble calcic carbonate ($CaCO_3$), and evaporated down in a silver basin.

(2.) By burning potassium in pure dry oxygen, and treating the oxides formed with water.

(3.) By igniting a mixture of nitre (1 part) and copper foil (3 parts) in a copper vessel, and dissolving the residue in water.

Properties.—Potassic hydrate is a very deliquescent solid, soluble in water with the evolution of heat, and, unlike most potassium compounds, soluble in alcohol. It has a strong caustic taste, and a nauseous smell. At a high temperature it is wholly volatile. The water of the hydrate cannot be expelled by heat. It must be regarded, therefore, as a *potassic hydroxide* (KHo) rather than as a *hydrate of potash* (K_2O, H_2O).

Caustic potash has an intensely alkaline reaction. It acts rapidly on all organic matters. It rapidly absorbs carbonic acid, hence one of its chief laboratory uses. It unites with silica when heated, forming potassic silicate. It decomposes the fixed oils, converting them into soaps; hence its use as *a lye* in soap making.

Tests for purity.—Pure potassic hydrate (1) is perfectly soluble in water and in alcohol; (2) gives no precipitate with *baryta water* (proving the absence of carbonates and sulphates); (3) gives no precipitate with *ammonic oxalate* (proving the absence of lime); (4) gives no precipitate with *argentic nitrate* in a solution neutralized with

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HNO_3 (proving the absence of chlorine); (5) gives no precipitate with *ammonic sulphide* (proving the absence of iron, etc.).

Purification.—The potash is dissolved in alcohol, and the clear solution evaporated to dryness. In this way the removal of potassic peroxide, carbonate, sulphate, and chloride, and also the silicates of lime, alumina, iron, and lead, all of which are insoluble in alcohol, may be effected. The solution in water must be preserved in glass *free from lead*, otherwise the lead oxide will be dissolved.

The liquor potassæ of the B.P. contains 6 per cent. of KHO (Sp. Gr. 1·058). The specific gravities of solutions of various strength are given in Table V. of the Appendix.

(5.) Potassic Chloride (KCl). *Sources.*—This salt is obtained from sea-water residue (Balard); also from the ashes of sea-weed (called "kelp"); also from the refuse of beet-sugar manufacture; also as a product of the potassic chlorate manufacture. It is also found as a natural product in the salt mines of Stassfurth, near Magdeburg (*Carnallite*; KCl, $MgCl_2$, $6H_2O$).

Properties.—The salt crystallizes in cubes. It is soluble in water (1 in 3). It fuses at a red heat, and is volatile above this temperature. It absorbs the vapor of SO_3, forming $KClSO_3$, which salt is decomposed by water. It is largely used in the nitre manufacture (see page 274). Its laboratory use depends on the insolubility of the double salt formed by it with platinic chloride in alcohol ($KCl,PtCl_4$).

(6.) Potassic Iodide (KI).

Preparation.—(1.) (α.) Iodine is added to a solution of caustic potash (KHO), a potassic iodide (KI) and a potassic iodate (KIO_3) being formed; thus—

$$6KHO + 3I_2 = 5KI + KIO_3 + 3H_2O.$$

Potassic hydrate + Iodine = Potassic iodide + Potassic iodate + Water.

(β.) This mixture is then heated, whereby the KIO_3 is reduced to KI, with the evolution of oxygen.

(2.) By dissolving potassic carbonate (K_2CO_3) in hydriodic acid.

$$K_2CO_3 + 2HI = 2KI + CO_2 + H_2O.$$

Potassic carbonate + Hydriodic acid = Potassic iodide + Carbonic anhydride + Water.

(3.) (α.) By digesting iron and iodine in water, a ferrous iodide (FeI_2) and a ferric iodide (Fe_2I_6) are formed;

(β.) To the boiling solution of these salts, potassic carbonate is added, carefully avoiding an excess.

$$FeI_2 + Fe_2I_6 + 4K_2CO_3 = 8KI + Fe_3O_4 + 4CO_2.$$

Ferrous iodide + Ferric iodide + Potassic carbonate = Potassic iodide + Magnetic oxide of iron + Carbonic anhydride.

The Fe_3O_4 is now filtered off, and the solution of KI evaporated down.

(4.) By adding potassic sulphate to baric or calcic iodide.

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Properties.—Potassic iodide is a white crystalline (cubic) solid, somewhat deliquescent, very soluble in water and in alcohol (1 part in 6). Its solution dissolves iodine. It is decomposed by nitric acid, chlorine, etc.

Test of purity.—There should be no change on adding hydrochloric acid to its solution. If the solution *turns brown*, potassic iodate (KIO_3) is present; if it *effervesces*, the presence of a carbonate is indicated.

(7.) **Potassic Bromide** (KBr). Its preparation is similar and its properties closely correspond to the iodide.

(8.) **Potassic Fluoride** (KF) is prepared by neutralizing HF with KHO.

(10.) **Potassic Fluosilicate** ($2KF,SiF_4$). This is the most insoluble of the potash salts. It is formed as a gelatinous precipitate, when hydro-fluosilicic acid ($2HF,SiF_4$) is added to a solution of a potassium salt. When dry it has the appearance of an earthy-looking powder.

(11.) **Potassic Cyanide** (KCy).

Preparation.—By fusing a mixture of potassic carbonate and potassic ferrocyanide.

$$2K_4FeCy_6 + 2K_2CO_3 = 10KCy + 3KCyO + Fe_2 + 2CO_2.$$

Potassic ferrocyanide + Potassic carbonate = Potassic cyanide + Potassic cyanate + Iron + Carbonic anhydride.

Properties.—A white, deliquescent, peculiar-smelling, alkaline salt, freely soluble both in water and in alcohol. It easily decomposes, liberating hydrocyanic acid (HCy). It melts at a low temperature, when it acts as a powerful *reducing* agent, owing to the ease with which it forms a cyanate (KCyO). Hence it is used as a flux.

(Thus: $PbO + KCy = KCyO + Pb$).

Its solution dissolves the insoluble silver salts; hence its use in photography and in electro-plating.

(12.) **Potassic Ferrocyanide,** *Yellow prussiate* ($K_4FeCy_6 + 3aq$).

Preparation.—By heating a mixture of potassic carbonate (K_2CO_3), iron, and nitrogenized organic matter. The fused mass is lixiviated (dissolved in water), and the clear solution crystallized.

Properties.—The salt has a yellow color, is permanent in air, and is decomposed by heat. It is insoluble in alcohol, but is soluble in water (1 in 4 at 60° F., and 1 in 2 at 212° F.).

It is used as a test re-agent, as a case hardener, and in the manufacture of Prussian blue.

(13.) **Potassic Ferricyanide,** *Red prussiate* ($K_3Fe'''Cy_6$).

Preparation.—By passing chlorine (avoiding excess) through a cold dilute solution of potassic ferrocyanide until it turns red.

Properties.—It is decomposed by an excess of chlorine, and by oxidizing agents, such as H_2S.

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COMPOUNDS OF POTASSIUM AND SULPHUR.

Dipotassic sulphide	K_2S.
Dipotassic disulphide	K_2S_2.
Dipotassic trisulphide	K_2S_3.
Dipotassic pentasulphide	K_2S_5.
Potassic sulphydrate	KHS.

(14.) Dipotassic Sulphide (K_2S).

Preparation.—By the action of KHO on KHS.

$$KHO + KHS = SK_2 + H_2O.$$

Potassic hydrate + Potassic sulphydrate = Dipotassic sulphide + Water.

(15.) Dipotassic Disulphide (K_2S_2), an orange-colored fusible solid.

(16.) Dipotassic Trisulphide (K_2S_3).

Preparation.—By passing CS_2 vapor over ignited potassic carbonate.

$$2K_2CO_3 + 3CS_2 = 2K_2S_3 + 4CO + CO_2.$$

Potassic carbonate + Carbonic disulphide = Dipotassic trisulphide + Carbonic oxide + Carbonic anhydride.

The "*hepar sulphuris*," or "*liver of sulphur*," is a compound of $3K_2S_3$ and K_2SO_4, and is prepared by fusing together sulphur and potassic carbonate.

$$4K_2CO_3 + 5S_2 = \underbrace{K_2SO_4 + 3K_2S_3}_{\text{Liver of sulphur}} + 4CO_2$$

Potassic carbonate + Sulphur = Liver of sulphur + Carbonic anhydride.

(18.) Dipotassic Pentasulphide, *Potassic Persulphide* (K_2S_5).

Preparation.—Either by the fusion of a solid sulphide, or by boiling a solution of a sulphide with an excess of sulphur.

Properties.—A deliquescent solid, forming when dissolved a deep yellow solution.

All the sulphides have an alkaline reaction, and a sulphuretted hydrogen odor. They all liberate sulphuretted hydrogen when treated with acids. On adding an acid, note, however, this distinction; that

(α.) With K_2S and KHS, *sulphuretted hydrogen* is evolved, and no sulphur is precipitated; but that

(β.) With the other sulphides, not only is *sulphuretted hydrogen* evolved, but *finely-divided white sulphur* is precipitated.

The higher sulphides, on exposure to air, become white from the formation of potassic thiosulphate ($K_2S_2O_3$), the excess of sulphur being liberated.

(19.) Potassic Sulph-hydrate, or *Potassic Hydric Sulphide* (KHS).

Preparation.—By saturating potassic hydrate (KHo) with sulphuretted hydrogen.

$$KHO + H_2S = KHS + H_2O.$$

Potassic hydrate + Sulphuretted hydrogen = Potassic sulph-hydrate + Water.

The solution turns yellow on exposure to air, and freely absorbs oxygen ($4KHS + O_2 = 2K_2S_2 + 2H_2O$).

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THE OXYSALTS OF POTASSIUM.

(20.) **Dipotassic Sulphate** (normal salt; K_2SO_4). *Properties.*—The crystals are six-sided prisms, soluble in water (1 in 12). The solution is neutral. The crystals decrepitate when heated.

(21.) **Hydric Potassic Sulphate;** *Potassic Bisulphate* (acid salt; $HKSO_4$). This salt is a residuary product of the nitric acid manufacture. The crystals are rhomboidal tables.

(22.) **Dipotassic Carbonate** (normal salt, K_2CO_3). *Preparation.*—(1.) Wood-ashes, which contain potassic carbonate, sulphate and chloride, are first of all lixiviated (*i.e.*, mixed with water). The clear solution is then evaporated until it begins to crystallize. The clear liquor, containing the more soluble potassic carbonate, is then poured off and boiled down in an iron-pot (hence the term pot-ash), and the residue calcined. This residue is known as "American ash" or "pearl-ash."

(NOTE.—The potassium is not present in the plant as potassic carbonate, but in combination with various organic acids. These salts are decomposed by heat, the hydrogen and excess of carbon passing off as H_2O and CO_2. Further, the younger the plant, the larger the yield of pot-ash.)

(2.) By deflagrating a mixture of cream of tartar and nitre.

Properties.—Potassic carbonate is a white deliquescent salt, crystallizing in oblique rhombic octahedra. It is soluble in water (1 in 1 aq.), the solution having an alkaline reaction. It melts at a red heat, and is slightly volatile at a higher temperature. When sand (SiO_2) is added to the melted salt, CO_2 escapes, and a potassic silicate is formed.

(23.) **Hydric Potassic Carbonate;** *Bicarbonate of Potash* ($HKCO_3$). *Preparation.*—By passing CO_2 through a solution of potassic carbonate (K_2CO_3).

Properties.—A neutral body crystallizing in right rhombic prisms, which are permanent in air. It is less soluble in water than K_2CO_3 (1 in 4). It fuses when heated, forming the normal salt. If a solution of the salt be boiled or exposed to the air, it loses one-fourth of its CO_2, and forms what is called the sesquicarbonate.

(24.) **Potassic Nitrate,** *Nitre* or *Saltpetre* (KNO_3), is obtained naturally, as an efflorescence, on the soil in India, and is prepared artificially in the nitre-plantations of Sweden (*see* page 274).

Properties.—A white crystalline solid. It is *dimorphous*, crystallizing both in rhombohedra and in six-sided prisms. It is insoluble in alcohol, but soluble in water (1 in 3·5). When heated to 674° F. (358° C.) it melts, the fused mass forming when cast into shape "*sal prunelle balls.*" When potassic nitrate is heated to redness, oxygen is evolved, and a potassic nitrite (KNO_2) formed; but when heated *above* this temperature, the nitrite itself is decomposed into O, N, and K_2O. When thrown on hot coal, the nitrate deflagrates. Paper

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saturated with a solution of the salt and dried, constitutes touch-paper. It is used in the gunpowder manufacture.

Gunpowder.

Composition.—A mixture of nitre, charcoal and sulphur in the following proportions:—

	English and Austrian.	Prussian.	Chinese.	French.
Nitre	75	75·0	75·7	75·0
Charcoal	15	13·5	14·4	12·5
Sulphur	10	11·5	9·0	12·5
	100·0	100·0	100·0	100·0

Nitre.—Sodic nitrate is never used in the manufacture of gunpowder on account of its being far more hygroscopic than potassic nitrate, and possessing much less powerful oxidizing properties. It is of importance that the nitre used should be free from sodic and potassic chlorides, as their presence in gunpowder render it liable to become damp.

Charcoal.—*Light wood charcoal*, such as that from the alder and willow, is the best adapted for the manufacture of gunpowder, owing to its very ready combustibility.

Sulphur.—The sulphur commonly used is *distilled*, and not *sublimed* sulphur. On mixing a quantity of the sulphur with water the solution should be barely acid to litmus, proving the absence of oxidized products. It should, when burnt, leave no ash. The *distilled* sulphur is the electro negative or soluble variety, but the *sublimed* sulphur contains a considerable quantity of the positive or insoluble variety. Hence the superiority of the distilled over the sublimed.

Properties.—Gunpowder is an angular grey solid, absorbing from 0·5 to 1·0 per cent. of moisture when exposed to the air. It explodes with difficulty by actual flame. It should, after firing, leave no residue, and moreover, it should not set light to a piece of paper on which it may be fired.

Decomposition.—When gunpowder is fired, nitrogen is set free, the carbon combining with the oxygen of the KNO_3 forming CO_2 and CO. Some of the CO_2 thus formed immediately combines with the potash to form K_2CO_3. The sulphur becomes oxidized to SO_3, and this also combining with potash forms K_2SO_4. Hence *the solids* formed by the explosion of gunpowder are potassic sulphate and potassic carbonate, and the *gases*, nitrogen, carbonic oxide, and carbonic anhydride.

$$4KNO_3 + C_4 + S = K_2SO_4 + K_2CO_3 + N_4 + 2CO_2 + CO.$$

Potassic nitrate + Carbon + Sulphur = Potassic sulphate + Potassic carbonate + Nitrogen + Carbonic anhydride + Carbonic oxide.

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Other bodies, however, such as K_2S, H_2S, and CH_4 are also formed.

Theory of gunpowder explosions.—The nitrogen and the carbonic anhydride set free by firing the powder, occupy at 0° C. and 30 B.P. 280 times the volume of the original powder; but this volume of gas is again expanded by heat to as much, probably, as five times its normal bulk.

(15.) Potassic Nitrite (KNO_2). This is prepared by heating potassic nitrate (see above). It is a white, crystalline, deliquescent salt.

(16.) Potassic Chlorate ($KClO_3$). *Preparation.*—(1.) By passing chlorine through a hot solution of potassic hydrate.

$$6KHO + 3Cl_2 = 5KCl + 5KClO_3 + 3H_2O.$$

Potassic hydrate + Chlorine = Potassic chloride + Potassic chlorate + Water.

The chlorate crystallizes out from the concentrated liquor, whilst the potassic chloride remains in solution owing to its much greater solubility.

(2.) By passing chlorine through milk of lime, whereby a calcic chlorate ($Ca2ClO_3$) and a calcic chloride ($CaCl_2$) are formed. Potassic chloride is then added to the solution. Thus:—

$$(Ca2ClO_3) + 2KCl = CaCl_2 + 2KClO_3.$$

Calcic chlorate + Potassic chloride = Calcic chloride + Potassic chlorate.

The chlorate is now crystallized out, the $CaCl_2$ being a very much more soluble salt than the chlorate.

Properties.—Potassic chlorate is a white crystalline solid (six sided prisms). It is not very soluble in water (1 in 16). It melts at 806° F. (430° C.), giving off oxygen, the residue consisting of *potassic perchlorate* ($KClO_4$) and *chloride*, which at a greater heat is entirely decomposed into potassic chloride and oxygen.

(17.) Potassic Perchlorate ($KClO_4$). (See above.)

(18.) Potassic Tartrate ($K_2C_4H_4O_6$) is prepared by boiling together cream of tartar and potassic carbonate.

(19.) Hydric Potassic Tartrate; *Potassic Bitartrate; Cream of Tartar.*—This is one of the most insoluble of potash salts. It is found deposited in casks used for the storage of wines.

(30.) Sodic Potassic Tartrate, *Rochelle salt* ($KNaC_4H_4O_6$), is prepared by boiling together cream of tartar and sodic carbonate.

(31.) Potassic Antimonious Tartrate, *Tartar emetic* ($K(SbO_2)$, $C_4H_4O_6$), is prepared by boiling together cream of tartar and antimonic oxide (Sb_2O_3).

Tests for Salts of Potassium.—*See* ANALYTICAL TABLES.

SODIUM (Na_2).

Na′=23. *Monad* (NaCl; ONaH.) *Specific gravity* 0·972. *Fuses at* 207·7° F.

History.—Discovered by Davy (1807).

Natural History.—It is found in animals, in vegetables (as in

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"barilla"), and in minerals. It occurs naturally as a chloride, carbonate, nitrate, sulphate and borate.

Preparation.—Its preparation is similar to that of potassium, viz., (1), by igniting a mixture of sodic carbonate and carbon; (2) by electrolysis; and (3) by the ignition of a mixture of sodic hydrate and metallic iron.

Properties.—(α.) *Physical.* A soft silvery white metal, burning with a *yellow* flame. It volatilizes more readily than potassium. Its spectrum consists of a yellow line at D.

(β.) *Chemical.* Sodium oxidizes rapidly and burns when heated. Its properties are similar to, but less energetic than, potassium.

Uses.—It is employed for the extraction of metallic aluminium and magnesium. (*See* Aluminium *and* Magnesium.) It is also used to extract gold and silver from their ores.

Compounds of Sodium.

	Names.	Formula (General.)	Formula (Constitutional).	Molecular Weight of Anhydrous Salts.	Specific Gravity of Crystals.	Contains Na_2O, or equal to Na_2O per cent. of Anhydrous Salt.
1	Sodic oxide (soda) ..	Na_2O	ONa_2	62		100·00
2	„ dioxide	Na_2O_2	O_2Na_2	78		79·48
3	„ hydrate (caustic soda)	NaHO	ONaH	40	2·13	77·5
4	Sodic chloride	NaCl	NaCl	58·50	2·24	Na=39·31
5	„ iodide	NaI	NaI	150	3·45	Na=15·33
6	„ bromide	NaBr	NaBr	103	3·08	Na=22·33
7	„ sulphate (Glauber's salt)	$Na_2SO_4,10H_2O$	$SO_2Nao_2,10OH_2$	142	1·469	43·67
8	Hydric sodic sulphate (bisulphate).. ..	$NaHSO_4$	SO_2HoNao	120	2·742	
9	Sodic sulphite.. ..	$Na_2SO_3,10H_2O$	$SONao_2,10OH_2$	126	1·736	
10	Hydric sodic sulphite	$NaHSO_3,4H_2O$	$SOHoNao,4OH_2$	104		
11	Sodic hyposulphite ..	Na_2SO_2	$SNao_2$	110		
12	„ thiosulphate ..	$Na_2S_2O_3,5H_2O$	$SS''ONao_2,5OH_2$	158	1·672	
13	„ carbonate ..	$Na_2CO_3,10H_2O$	$CONao_2,10OH_2$	106	1·423	58·49
14	Hydric sodic carbonate (bicarbonate) ..	$NaHCO_3$	$COHoNao$	84	2·192	36·90
15	Sodic nitrate (cubic nitre)	$NaNO_3$	NO_2Nao	85	2·26	
16	Trisodic phosphate (sulphosphate) ..	$Na_3PO_4,12H_2O$	$PONao_3,12OH_2$	164	1·618	
17	Hydric disodic phosphate (rhombic) ..	$Na_2HPO_4,12H_2O$	$POHoNao_2,12OH_2$	142	1·525	43·66
18	Sodic dihydric phosphate	$NaH_2PO_4H_2O$	$POHo_2Nao,OH_2$	120		
19	Sodic pyrophosphate (tetrasodic phosphate)	$Na_4P_2O_7,10H_2O$	$P_2O_3NaO_4,10OH_2$	266	1·836	
20	Sodic metaphosphate	$NaPO_3$	PO_2Nao	102		30·39
21	„ diborate (borax)	$Na_2O,2B_2O_3,10H_2O$	$B_4O_5Nao_2,10OH_2$	202	1·73	30·69

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COMPOUNDS OF SODIUM WITH OXYGEN AND HYDROXYL.

Sodic oxide	Na_2O.
Sodic dioxide	Na_2O_2.
Sodic hydrate	NaOH.

(1.) Sodic Oxide; *Soda* (Na_2O). *Preparation.*—By burning the metal in oxygen or in dry air. (The product contains more or less Na_2O_2.) *Properties.*—A yellowish white body, very deliquescent, forming NaHO when dissolved in water.

(2.) Sodic Dioxide (Na_2O_2). *Preparation.*—By heating sodium to 392° F. (200° C.) in a current of dry air. *Properties.*—It is a white solid when cold, and yellow when hot. On heating its solution in water, oxygen is expelled.

(3.) Sodic Hydrate; *Caustic Soda* (NaHO). For its preparation *see* Potassic hydrate, to which it is in all respects similar (page 291).

Preparation.—(*Commercial.*) Caustic soda is largely prepared from the *red liquor* of the alkali works (*see* page 303). The solution of the black ash is concentrated to 1·5 specific gravity, the sodic carbonate, sulphate and chloride crystallizing out in the course of the evaporation. The liquor left constitutes "*red liquor*" which retains the sodic hydrate, owing to its greater solubility. Certain other compounds are present in small quantity, such as the sulphides of iron and sodium, to which the peculiar red color of the liquor is due. The hot liquor is now treated either with sodic nitrate and a current of air, or with sodic nitrate only, in order to oxidize the sulphides present, ferric oxide being deposited. The solution is then evaporated until the sodic hydrate is obtained as a fused mass.

Kryolite ($3NaF,AlF_3$) is also employed in the preparation of sodic hydrate by decomposing it with calcic hydrate.

Properties.—Sodic hydrate is a white fusible deliquescent substance. By exposure to air it first becomes liquid from absorbing water, and afterwards dries up from absorbing carbonic anhydride.

It acts rapidly on organic structures. It is largely used both in the manufacture of *hard soap* (*i. e.*, caustic soda and fat or oil), and of *marine soap* (*i. e.*, caustic soda and cocoa-nut oil).

For the specific gravity of solutions of different strength, *see* Table VI., in Appendix.

COMPOUNDS OF SODIUM AND THE HALOIDS.

(4.) Sodic Chloride; *Common salt; Muriate of soda* (NaCl). *Sources.*—(1.) From *beds of "rock salt,"* such as are found at Northwich, Cardona, Wielitzka, etc. Rock salt often occurs of a red tint, from the presence of iron. The perfectly white crystallized specimens occasionally found are known as "*sal gem.*"

(2.) *Sea water.*—The salt obtained from this source is called *Bay Salt.*

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The solution that remains after the extraction of the salt is called "*bittern.*"

(3.) *Salt springs;* also *rivers, lakes, soils,* etc.

Preparation.—The salt is crystallized from its solution, the details of the process varying in different countries. In the case of salt mines, it has been found more economical to pump water into the mine, and to pump it up again when saturated with the salt, than to raise the solid salt itself from the mine.

(α.) Sometimes the water is evaporated at once by boiling.

(β.) Sometimes the brine, if dilute, is first of all concentrated, by allowing it to flow several times from a height over brushwood freely exposed to the air (*graduation*), and when the solution has attained a gravity of 1·14 effecting its further concentration by heat (France and Germany).

(γ.) In *cold* climates the salt water is run into open reservoirs, and allowed to freeze. The solid ice, which contains very little salt, is then removed, thereby concentrating the remaining solution, which is finally evaporated to dryness (Russia).

(δ.) In *hot* climates the sea-water is allowed to evaporate spontaneously in shallow reservoirs, when what is called "*bay salt*" is deposited. The salt prepared from sea-water always contains magnesic chloride, which may to a certain extent be separated from the sodic chloride by exposure to air, and by washing, owing to the greater deliquescence of the magnesic chloride. The liquor remaining after the sodic chloride is removed, is called "bittern," and is employed as a source of magnesia and bromine.

We may here note that every 1000 parts of sea-water contains

29·0 parts of Chloride of sodium (=4 ozs. of salt per gallon, or 1 bushel in 300 to 350 gallons of water).
0·5 ,, ,, Chloride of potassium.
3·0 ,, ,, Chloride of magnesium.
2·5 ,, ,, Sulphate of magnesia.
1·5 ,, ,, Sulphate of lime.

Properties.—Common salt is a crystalline (cubic) non-deliquescent solid. The presence of magnesic chloride renders it deliquescent. A clear colorless specimen of salt is *diathermanous*, that is, it allows the *heat* rays to pass as well as the *light* rays. Water is non-diathermanous, glass holding an intermediate position in this respect between water and salt. Common salt is insoluble in absolute alcohol, but is soluble in dilute alcohol and also in water (1 part in 3), and about equally at all temperatures, a saturated solution having a specific gravity of 1·205. The crystals decrepitate when heated. At a bright red heat they fuse, and at a stronger heat vaporize.

Uses.—It is used for dietetic and culinary purposes, as *e. g.*, for curing meats, owing to its antiseptic action. It is also used in

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agriculture, in earthenware glazing, etc., and also very largely in the carbonate of soda manufacture.

(5.) **Sodic Iodide** (NaI). (Vide *Potassic Iodide,* to which it is closely analogous.)

(6.) **Sodic Bromide** (NaBr). (Vide *Potassic Bromide.*)

Sodium Oxy-Salts.

(7.) **Sodic Sulphate;** *Glauber's salt* ($Na_2SO_4,10H_2O$). This salt is formed in the first stage of the sodic carbonate manufacture by the action of sulphuric acid on common salt (*see* page 302), the product being commonly known as "*salt cake.*"

It occurs naturally in many waters, as in the Cheltenham springs; in certain minerals, as Thénardite, Glauberite ($Na_2SO_4,CaSO_4$), etc.; and also as a common efflorescence on brick walls.

Properties.—A colorless salt, having a bitter taste and a purgative action. It crystallizes in oblique rhomboid prisms, or in forms derived therefrom. The crystals are efflorescent, giving off the whole of their water at common temperatures. The salt melts in its own water of crystallization when heated.

Its solubility in water is remarkable. A hot saturated solution, on being cooled without disturbance and out of contact with air, does not crystallize; whilst on the admission of air to the cold solution, its immediate crystallization may be effected. The explanation of this circumstance is that probably the salt in the supersaturated solution exists in the anhydrous form, whilst when it separates, it crystallizes out with the ten molecules of water of crystallization. We must here note that sodic sulphate has been prepared in two forms at least, their solubilities differing very remarkably. Thus—

(α.) The solubility of the salt Na_2SO_4 decreases from 64·2° F. (17·9° C.) to 217·5° F. (103·1° C.).

(β.) The solubility of the salt $Na_2SO_4,10H_2O$ increases up to 93·1° F. (33·9° C.) (100 aq. dissolves 117·9 parts).

Sodic sulphate is soluble in hydrochloric acid, its solution being accompanied with a great depression of temperature.

(8.) **Hydric Sodic Sulphate;** *Acid sodic sulphate; Bisulphate of soda* ($NaHSO_4$).

Preparation.—By adding seven parts of sulphuric acid to ten parts of the anhydrous normal salt, and evaporating.

Properties.—A non-deliquescent, very soluble, acid salt, forming the neutral sulphate when heated.

(9.) **Sodic Sulphite** ($Na_2SO_3,10H_2O$).

Preparation.—By passing SO_2 over crystals of Na_2CO_3.

Properties.—The salt crystallizes in oblique prisms, which are efflorescent and fuse at 113° F. (45° C.). It is soluble in water (1 in 4), the solution having an alkaline reaction. It evolves sulphurous

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acid when treated with HCl or with H_2SO_4. It is used as a bleaching agent, and as an "antichlor."

(10.) Hydric Sodic Sulphide, *Acid sulphite* or *Bisulphite* of soda ($NaHSO_3$), has also been prepared.

(11, 12.) Sodic Hyposulphite and **Thiosulphate** (*see* p. 271).

(13.) Sodic Carbonate; *Common washing soda; Scotch soda*—($Na_2CO_3,10H_2O$).

Preparation.—Before the year 1823, this salt was prepared from the ashes of sea-weed, known as "kelp," "*barilla*," or "*varec*," one-fourth the weight of which consists of sodic carbonate. The kelp was mixed with water, and the clear solution concentrated by heat. The sodic carbonate crystallized out first, leaving the iodine compounds in solution, owing to their much greater solubility.

Since 1823, sodic carbonate has been prepared from common salt by the process of Lablanc. This process may be described as taking place in three stages as follows:—

(α.) A mixture of common salt and oil of vitriol is first heated in a reverberatory furnace, whereby sodic sulphate is formed. This constitutes what is called "*salt cake*."

$2NaCl$	+	H_2SO_4	=	Na_2SO_4	+	$2HCl$.
Sodic chloride	+	Sulphuric acid	=	Sodic sulphate (*salt cake*)	+	Hydrochloric acid.

[It has been suggested to use sulphurous acid, steam and air, in the place of sulphuric acid. (Hargreave.) $2NaCl+H_2O+SO_2+O=Na_2SO_4+2HCl$.]

(β.) The salt cake thus formed is now mixed with limestone and small coal, and again heated. The following changes occur:—(1.) The carbon reduces the sodic sulphate to sodic sulphide, carbonic anhydride being set free ($Na_2SO_4+C_2=NaS+2CO_2$). (2.) The carbon acting on the calcic carbonate, sets free carbonic oxide and lime ($CaCO_3+C=2CO+CaO$). (3.) The lime reacts on the sodic sulphide in the presence of carbonic anhydride, producing sodic carbonate, which is soluble, and calcic sulphide, which is insoluble—

$$(Na_2S+CaO+CO_2=Na_2CO_3+CaS).$$

The reaction in full may be thus stated:—

Na_2SO_4	+	$4C$	+	$CaCO_3$	=	CaS	+	$4CO$	+	Na_2CO_3.
Sodic sulphate	+	Carbon	+	Calcic carbonate	=	Calcic sulphide	+	Carbonic oxide	+	Sodic carbonate.

The black mass formed consists of an excess of chalk and coal, together with caustic soda (formed by the action of the lime on the sodic carbonate), calcic sulphide, and sodic carbonate. It constitutes what is commonly known as "*black ash*" or "*ball soda*."

(γ.) The black ash is now treated with water to dissolve out the sodic carbonate. The clear solution is poured off, and evaporated to dryness, the solid residue of sodic carbonate constituting what is known as "*soda ash*."

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Impurities of Soda Ash.—Sodic chloride, sodic sulphate, and sodic hydrate.

Purification of the Soda Ash.—The soda ash is first mixed with sawdust, and heated, whereby any sodic hydrate is converted into sodic carbonate by the action of the carbonic anhydride, formed from the burning of the carbonaceous matter. The mass is then treated with water, and the filtered solution evaporated down and crystallized.

Very often, however, the clear solution of the "black ash," is at once concentrated by heat until the Na_2CO_3 is deposited, the mother liquor, known as "*red liquor*," being used in the preparation of sodic hydrate (*see* page 299).

Waste Products.—Hydrochloric acid is set free in the formation of the salt cake. If this were allowed to escape it would prove a nuisance. Hence in alkali works, it is usually absorbed by means of a wet coke scrubber. The liquid hydrochloric acid of commerce, used largely in the manufacture of bleaching-powder, etc., is commonly prepared in this manner.

Soda or Alkali Waste.—It will be noted that nearly all the sulphur of the sulphuric acid used, forms the insoluble calcic sulphide of the black ash, which, together with the excess of coal and lime, after its thorough exhaustion with water, forms the "soda," "alkali," or "tank waste." A part of this is now used in the preparation of hyposulphite of soda (sodic thiosulphate), (*see* page 272), whilst the sulphur of the remaining portion is recovered by blowing air in such quantity through the moist material that a calcic persulphide and thiosulphate may be formed (Mond's Process). From this yellow liquor the sulphur is thrown down by adding hydrochloric acid:—

(1.) $12CaS + 6O_2 = 2CaS_5 + CaS_2O_3 + 9CaO.$

Calcic sulphide + Oxygen = Calcic persulphide + Calcic thiosulphate + Calcic oxide.

(2.) $2CaS_5 + CaS_2O_3 + 6HCl = 3CaCl_2 + 3H_2O + 6S_2.$

Calcic persulphate + Calcic thiosulphate + Hydrochloric acid = Calcic chloride + Water + Sulphur.

Another process adopted for the recovery of the sulphur, is by adding to the soda-waste the liquor from chlorine stills (containing $MnCl_2$ and Fe_2Cl_6), whereby calcic chloride, and the sulphides of iron and manganese are formed; these latter, on exposure to the air, become converted into oxides with the consequent separation of the sulphur:—

(1.) $\underbrace{MnCl_2 + Fe_2Cl_6}_{\text{Chlorine-still liquor}} + 4CaS = MnS + Fe_2S_3 + 4CaCl_2.$

+ Calcic sulphide = Manganese sulphide + Iron sulphide + Calcic chloride.

(2.) $2MnS + O_3 = Mn_2O_3 + S_2;\quad 2Fe_2S_3 + 2O_3 = 2Fe_2O_3 + 3S_2.$

Manganese sulphide + Oxygen = Manganese oxide + Sulphur; Iron sulphide + Oxygen = Iron oxide + Sulphur.

Properties.—Sodic carbonate forms efflorescent crystals, which

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melt when first heated in their water of crystallization, but ultimately leave the anhydrous salt, Na_2CO_3. At a red heat this salt melts without decomposing. It has an alkaline taste and reaction, and is very soluble in water (1 in 2 at 60° F., and 1 in 1 at 212° F.).

(N.B. Sodic carbonate is an *efflorescent* salt, whilst potassic carbonate is a *deliquescent* salt.)

(14.) Hydric Sodic Carbonate; *Bicarbonate of soda* ($NaHCO_3$).

Preparation.—By exposing the moist crystals of the normal salt (Na_2CO_3) to the action of carbonic anhydride, or by saturating a solution of the salt with the gas. Considerable heat is evolved during the process.

Properties.—Bicarbonate of soda is less soluble than the normal salt (1 in 10 aq. at 50° F.). In preparing the salt from the carbonate a sesquicarbonate is first formed, then a bicarbonate. Similarly by heating a solution of the bicarbonate a sesquicarbonate is first formed (1), and then a carbonate (2).

(1.) $4NaHCO_3 = 2Na_2CO_3,H_2CO_3 + H_2CO_3.$

(2.) $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$

The carbonate of soda used in medicine is a bicarbonate, in other words a hydric sodic carbonate ($NaHCO_3$). It is not so soluble as the carbonate, and exhibits a very slightly alkaline reaction to turmeric, whereas the carbonate is very alkaline.

(15.) Sodic Nitrate; *Cubic Nitre; Chili saltpetre* ($NaNO_3$). Found native. It crystallizes in rhombohedra, the crystals being deliquescent and very soluble (1 in 2 aq.). It fuses at 591° F. (310·5° C.) and is decomposed at higher temperatures. It is used in the manufacture of nitric and sulphuric acids, and also in the preparation of potassic nitrate for gunpowder (see page 274). It is further employed as a dressing for soils.

(16.) Sodic Biborate; *Borax* ($Na_2O, 2B_2O_3, 10H_2O$).

Preparation.—The crude borax (tincal), a compound of soda and boracic acid, was originally imported from Thibet, where it occurs as a natural production in the residue obtained from the evaporation of the water of certain lakes. It is usually prepared at the present time by fusing sodic carbonate with boracic acid, the latter acid expelling the carbonic anhydride from the sodic carbonate. The residue is then dissolved and crystallized.

Properties.—It forms hard clear prismatic efflorescent crystals, the transparency of which is soon destroyed by exposure to air. The solution (1 in 12 aq.) is alkaline. When heated the crystals at first intumesce (swell up), then fuse to a colorless liquid, which, on cooling, has the appearance of a glassy mass (vitrified borax). Fused borax possesses the power of dissolving many metallic oxides. Hence its use as a reagent in blowpipe analysis, the oxides imparting special colors to the borax bead, by which they may be recognised. It is

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also used for a similar reason, to remove any traces of oxide (or tarnish) from the surface of metals before soldering. It is employed, moreover, as a flux; also in enamelling (to render the enamels more fusible), in fixing colors on porcelain, in glazing stoneware, and also in medicine.

THE PHOSPHATES (see page 134).

(17.) Hydric Sodic Phosphate.—*Phosphate of soda*—(Na_2HPO_4, $12H_2O$).

Preparation.—By adding sodic carbonate to the tetrahydric calcic phosphate obtained during the process of preparing phosphorus.

$H_4Ca2PO_4 + 2Na_2CO_3 = CaCO_3 + H_2O + CO_2 + Na_2HPO_4$

Tetrahydric calcic phosphate + Sodic carbonate = Calcic carbonate + Water + Carbonic anhydride + Hydric sodic phosphate.

$P_2O_2Ho_4Cao'' + 2CONao_2 = COCao'' + OH_2 + CO_2 + PONao_2Ho$

Properties.—The crystals are *rhombic*, efflorescent, and soluble in cold water (1 in 4).

Action of heat.—When heated to 99° F. (37·2° C.) the crystals melt in their own water of crystallisation. Heated to 212° F. (100° C.) they lose their 12 molecules of water, becoming Na_2HPO_4. At a red heat they lose one more molecule of water, *sodic pyrophosphate* ($Na_4P_2O_7$) being formed. If free phosphoric acid (H_3PO_4) be added to this salt ($Na_4P_2O_7$), the *biphosphate of soda* or *sodic dihydric phosphate* is formed (NaH_2PO_4, H_2O). Phosphate of soda has an acid reaction.

The *tribasic* phosphates of soda (and the biphosphate of soda) give *yellow* precipitates with argentic nitrate.

(19.) Sodic Pyrophosphate ($Na_4P_2O_7$,$10H_2O$) (see above) crystallises in prisms. Its solution is alkaline.

The *tetrabasic* pyrophosphate gives a *white* precipitate with argentic nitrate, which is not changed by exposure to light.

(20.) Sodic Metaphosphate, or **Monophosphate** ($NaPO_3$).

Preparation. — By heating either the sodic dihydric phosphate (NaH_2PO_4) or microcosmic salt to redness.

Properties.—A non-crystalline, deliquescent, very soluble substance, the solution having a feebly acid reaction.

The *monobasic* phosphate gives a *white gelatinous* precipitate with argentic nitrate.

Silicates of Sodium.

Silica or silicic acid has the power of expelling carbonic anhydride from its compounds. Hence various silicates may be formed by fusing silica with sodic carbonate.

The salt $Na_2O,SiO_2,9H_2O$ (Futsche) may be prepared by fusing 2 parts of powdered flint with 3 parts of sodic carbonate.

The salt $Na_2O,36SiO_2$ (Forchhammer) may be prepared by boiling finely divided silica in a saturated solution of sodic carbonate.

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There are, moreover, many other silicates. The silicate $Na_2O,4SiO_2$ or "*soluble glass*" is prepared by fusing 15 parts of sand with 8 parts of sodic carbonate and 1 part of charcoal (Fuchs). The silica expels the CO_2, its liberation being assisted by the carbon which converts it into carbonic oxide. The mass is insoluble in cold water, but is soluble in hot (1 in 5 aq.) The solution is alkaline.

It is used for stone preservation, in fresco-painting (Stereochromy), as a dung substitute in calico-printing, etc.

Glass.

Glass is a compound of an alkaline silicate, and a silicate of an alkaline earth, mixed with one or other of the metallic oxides. It is not, however, a true chemical compound but a simple mechanical mixture. The following table represents the percentage composition of different glasses.

	Window.	Plate.	Crown for optical purposes.	English flint.
Silica	66·37	73·5	62·5	51·93
Potash..	..	5·5	22·5	13·77
Soda	14·23	12·0	..	..
Lime	11·86	5·5	12·5	..
Alumina	8·16	3·5	2·5	0·47
Oxide of lead..	..	..	..	33·28
Oxide of iron and manganese ..	..	..	..	0·25

Soda always imparts a slightly green tinge to glass, which does not occur with potash. A soda glass, however, is more fusible and more brilliant than a potash glass.

Lime diminishes the fusibility of the glass, imparts no color, and increases its hardness and lustre. If an excess be used, however, the glass on cooling turns milky.

Lead increases the fusibility and the lustre of the glass, and renders it softer.

Baryta is also said to increase its fusibility.

Window glass consists of the silicates of soda, lime and alumina. 100 parts of sand, 35 to 40 of chalk, 30 to 35 of soda ash, and 50 to 150 of "*cullet*" or broken glass, are first subjected to a low heat, so as to expel any moisture present, and also to drive off a certain quantity of carbonic acid to prevent subsequent frothing. The heat is then sufficiently raised to effect the complete fusion of the materials. Sometimes sodic sulphate is used instead of sodic carbonate (soda ash), the sulphuric anhydride being expelled by the silica, as SO_3. Sometimes a little charcoal is added, whereby the SO_3 is reduced to SO_2, its

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expulsion being thus effected at a lower temperature. After melting, the mixture is allowed to remain for the "glass gall," or "sandiver," or "scum" (Na_2SO_4 and NaCl) to collect, which is then skimmed off.

Plate-glass consists of the silicates of soda, lime and potash; 300 parts of pure white sand, 100 of sodic carbonate, 43 of slaked lime, and 300 of fragments of glass are the proportions of the several constituents employed in its manufacture.

Crown-glass, for optical purposes, contains no soda, in order to avoid the green tint that the alkali imparts to the glass. Sometimes a little boracic acid is used in the place of a portion of the silica.

Wine-bottle and *carboy glass* consists of the alkaline silicates and the silicates of lime and alumina, with oxide of iron. The constituents are 100 parts of common red (ferruginous) sand, 80 of soap-maker's waste, 80 of gas lime, 5 of clay, and 3 of rock salt.

Flint-glass (crystal).—The constituents of flint-glass are 300 parts of pure white sand, 200 of minium (red oxide of lead), 100 of refined pearlash, and 30 of nitre. The nitre is added in order to prevent the reduction of the lead, by oxydizing any matters that might otherwise effect it. The fusion of the materials is, for the same reason, carried on in a closed pot. No soda is used because of the tint it imparts to the glass, whilst lead is added in order to increase its fusibility and its refractive and dispersive power. Crystal is easily scratched and is disposed to tarnish and to change colour.

Bohemian glass consists chiefly of potassic and calcic silicates.

Devitrification.—Reaumur's porcelain glass is prepared by heating certain kinds of glass, such as bottle-glass, or the soluble soda-glass of Fuchs, to very nearly its melting-point, and then slowly cooling, whereby it is changed into a hard, opaque, porcelain-like mass (devitrification), a change due to the separation and crystallization of the silicates. Its original transparent state may be restored by fusion. Such glass is less fusible than common glass, and is a fair conductor of electricity.

Enamelling is effected by diffusing certain white opaque substances, such as stannic or antimonious oxides through the glass.

Colouring.—This is effected by dissolving certain metallic oxides in the glass. The glass generally used for this purpose contains a little borax and about 53 per cent. of oxide of lead (paste or strass). Ferrous oxide imparts a *green* color; oxides of silver and antimony, a *yellow;* finely-divided charcoal, a *brownish yellow;* uranic oxide, a *greenish opalescent yellow;* cupric oxide (CuO) or chromic oxide an *emerald green;* cuprous oxide (Cu_2O), a *ruby-red;* gold and stannic oxide, a more brilliant *ruby-red;* manganic sesquioxide a *violet;* oxide of cobalt, a *blue;* oxides of cobalt and manganese, a *black.*

It will be remarked that whilst ferrous oxide imparts a green color to glass, ferric oxide imparts no color. Hence a little nitre or arse-

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nious acid, or Pb_3O_4, is often added to the glass, in order to oxidize any ferrous oxide that may be present. Similarly, the black oxide of manganese is sometimes used, which converts the ferrous oxide into ferric oxide, the manganese oxide becoming a protoxide, which, like ferric oxide, imparts no color to the glass.

Painting on Glass is effected by painting with a very fusible glass, in a state of fine powder mixed up with turpentine and the oxide requisite to impart the color, on a somewhat non-fusible glass. A sufficient heat is then applied to melt the fusible glass paint.

Colored Glass is generally flashed, that is, colored only on the surface by dipping the uncolored glass into the colored glass pot.

Tests for Sodium Compounds.—(*See* ANALYTICAL TABLES.)

LITHIUM (Li_2).

Li'=7. *Monad* (LiCl — **O**LiH—). *Specific gravity*, 0·593. *Fuses at* 356° F. (180° C.).

History.—(λιθος, a stone). Lithia was discovered by Arfvedson (1817). The metal was first prepared in small quantities by Davy, and in bulk by Matthiessen (1855).

Natural History.—It is a widely, but sparingly-distributed metal. It is found in all three kingdoms of nature. In the (*α.*) *animal*, it occurs in milk and in human blood; in the (*β.*) *vegetable*, in tobacco; in the (*γ.*) *mineral*, in all waters, also in lepidolite, petalite, triphane (spodumene), triphylline, etc.

Preparation.—By the electrolysis of fused lithic chloride.

Properties.—(*α.*) *Physical.* Lithium is a white metal, and is the lightest metal known. It is very ductile and volatile, and burns with a brilliant *crimson* flame.

(*β.*) *Chemical.* Its reactions are similar to those of sodium and potassium, but it is less readily oxidized. Like sodium, it decomposes water at ordinary temperatures, but it does not inflame.

Uses.—Its salts are used in gout as a solvent for uric acid.

LITHIUM COMPOUNDS.

The Lithium compounds best known are the following:—

Lithia (Li_2O); *lithic hydrate* (LiHO) a body which rapidly corrodes platinum; *lithic sulphate* (Li_2SO_4,H_2O) a crystalline soluble salt; *trilithic phosphate* (Li_3PO_4) a salt soluble in dilute acids, but insoluble in alkaline solutions or in solutions of alkaline phosphates; and *lithic carbonate* (Li_2CO_3) a very sparingly soluble salt.

Tests for the Salts of Lithium.

(1.) The salts commonly are fusible and deliquescent.

(2.) They communicate a red color to the blowpipe flame.

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(3.) They give a non-continuous spectrum showing a crimson band between B and C and a faint band in the orange.

(4.) They corrode platinum foil when heated upon it.

(5.) *Potassic carbonate* gives a white precipitate of lithic carbonate in cold and very concentrated solutions.

(6.) *Hydric disodic phosphate* gives a white precipitate in a neutral or an alkaline solution, soluble in acids and in ammonium salts.

CÆSIUM, Cs=133; RUBIDIUM, Rb=85·4.

History.—These metals were discovered by Bunsen and Kirchhoff (1860) by spectrum analysis.

Natural History.—They are found in the *vegetable* kingdom (tobacco, coffee, grapes, beetroot), and in the *mineral*, as *e.g.*, in many mineral waters.

Properties.—*Cæsium* gives two blue lines in the spectrum (*cæsius* sky-blue.) *Rubidium* is a white, rapidly oxidizable metal evolving a greenish-blue gas (Sp. Gr. 1·52°; fuses at 101·3 F., 38·5° C.) It is known by its *red* spectrum lines (*rubidus* dark red.)

Compounds of Cæsium and Rubidium.

The compounds of cæsium best known are as follows:—

Cæsic oxide (cæsia, Cs_2O); *cæsic hydrate* (CsHO); *cæsic chloride* (CsCl); *cæsic sulphate* (Cs_2SO_4), a body forming double salts with sulphates of the class to which magnesic sulphate belongs; a *hydric cæsic sulphate* ($CsHSO_4$); *cæsic nitrate* ($CsNO_3$); *cæsic carbonate* and an *acid carbonate* (Cs_2CO_3 and $HCsCO_3$).

Similar rubidium salts have also been prepared.

The peculiar spectra of cæsium and rubidium constitute their distinctive tests.

AMMONIUM $(NH_4)_2$.

Ammonium is a hypothetical metal, of which a supposed amalgam has been prepared. (See page 221.)

Preparation.—(1). By electrolysing ammonic chloride, a globule of mercury forming the negative terminal.

(2). By placing a potassic amalgam in a warm solution of ammonic chloride.

In these cases the mercury swells enormously, owing, it is believed, to the formation of an amalgam with the metal NH_4. The ammonium amalgam, however, rapidly decomposes into Hg,NH_3 and H, the two last gases being in the proportion of $2NH_3$ to H_2.

The ammonium theory depends largely on the circumstance that the combination of dry ammonia-gas (NH_3) with the anhydrides, such as CO_2,SO_3, etc., form a class called the *ammonides*, which have but

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a very slight resemblance indeed to the corresponding soda or potash salts. Thus *sulphuric ammonide* [$(NH_3)_2SO_3$] is a soluble crystalline body, but its solution is not precipitated by baric chloride as true sulphates are, nor by platinic chloride as true ammonium salts are. By long boiling, however, the *sulphuric ammonide* [$(NH_3)_2SO_3$] becomes *ammonic sulphate* [$(NH_4)_2SO_4$] the change really consisting in the assimilation of one molecule of water by two ammonia molecules (*i.e.* $2NH_3+H_2O=2NH_4O$). In the case, however, of the hydracids, a true ammonium salt (as NH_4Cl) is formed independently of a water molecule, the hydrogen of the hydracid itself supplying the hydrogen atom required to form the ammonium radical.

Again, carbonic anhydride and dry ammonia-gas combine to form a white volatile compound [$(NH_3)_2CO_2$], which is ammonic carbonate *minus* a water molecule, and is regarded as an ammonic salt of carbamic acid (H_2CO_2, or $COHo_2$), a derivative of carbonic acid, where one of amidogen (NH_2) in the salt is substituted for one of the group hydroxyl of the acid. If both hydroxyl groups in the carbamic acid be replaced by amidogen, a body called carbamide [$(NH_2)_2CO$] is then formed.

Compounds of the Hypothetical Metal Ammonium.

		Names.	Formula (general).	Formula (constitutional).	Molecular Weight.	Specific Gravity.	NH_3 per cent.
1		Ammonic hydrate (ammonia)	$(NH_4)HO$	AmHo	35		
2		Ammonic chloride (sal ammoniac)	NH_4Cl	AmCl	53·5	1·578	31·78
3		Ammonic iodide	NH_4I	AmI	145		11·72
4		Ammonic bromide ..	NH_4Br	AmBr	98		17·34
5	Sulphides.	Diammonic sulphide ..	$(NH_4)_2S$	SAm_2	68		
6	Sulphides.	Diammonic disulphide .	$(NH_4)_2S_2$	S_2Am_2	100		
7	Sulphides.	Diammonic pentasulphide	$(NH_4)_2S_5$	S_5Am_2			
8	Sulphides.	Diammonic heptasulphide	$(NH_4)_2S_7$	S_7Am_2	260		
9	Sulphides.	Ammonic hydric sulphide	NH_4HS	SHAm	51		
10		Ammonic sulphate ..	$(NH_4)_2SO_4$	SO_2Amo_2	132	1·695	25·75
11		Hydric ammonic sulphate	$(NH_4)HSO_4$	SO_2HoAmo	115		
12		Sodic ammonic sulphate	$NH_4NaSO_42H_2O$				
13	Carbonates.	Ammonic carbonate ..	$(NH_4)_2CO_3$	$COAmo_2$			
14	Carbonates.	Ammonic sesquicarbonate	$2(NH_4)_2O,3CO_2$		236		
15	Carbonates.	Ammonic bicarbonate..	NH_4HCO_3	COHoAmo	79	1·586	
16		Ammonic nitrate.. ..	NH_4NO_3	NO_2Amo	80	1·635	
17		Sodic ammonic hydric phosphate (microcosmic salt)	$NaNH_4HPO_4,4H_2O$	POHoAmoNao	137		

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(1.) **Ammonic Hydrate.**—*Ammonia* (H_4NHO). This is an aqueous solution of ammonia gas. When the liquid is heated, ammonia is expelled. Hence, supposing the existence of a hydrate, the affinity must be of a very feeble nature.

(2.) **Ammonic Chloride.**—*Sal ammoniac; Muriate of ammonia* (NH_4Cl).

Preparation.—By the combination of ammonia and hydrochloric acid gases. In commerce it is prepared from gas liquor, which contains ammonia (derived from the nitrogen of the coal) as a carbonate and as a sulphide. The ammoniacal liquor is first neutralised with HCl, and the salt crystallised out and purified by distillation, or else ammonia gas is set free by heating the liquor with lime, the free ammonia being conveyed into hydrochloric acid.

Properties.—It is a white solid, crystallising in cubes and octahedra. It has no smell. It is slightly soluble in alcohol, but very soluble in water (1 in 3 at 60° F., and 1 in 1 at 212° F.). It is slightly acid to litmus. It is volatile by heat without fusing, undergoing a *temporary* decomposition when heated to a certain temperature, into hydrochloric acid and ammonia (*dissociation*). Hence the vapor volume of this, as well as of several other ammonium salts, is double that of most compounds. The relative weight of the vapor is 13·3, so that one molecule (53·5 parts) instead of occupying two volumes would seem to occupy four.

(3, 4.) The **Ammonic Iodide** (NH_4I) and **Bromide** (NH_4Br) are used in photography. They are both soluble salts, the former decomposing rapidly by exposure to air.

(5-8.) **Sulphide of Ammonium.**—*Diammonic sulphide* or *protosulphide* [$(H_4N)_2S$].

Preparation.—(1.) By distilling together ammonic chloride and potassic sulphide; and collecting the products in a cold receiver.

(2.) By mixing H_2S with twice its volume of ammonia gas.

Properties.—It consists of colorless crystals. It is a very unstable body, becoming at ordinary temperatures ammonia and ammonic-hydric sulphide.

Diammonic Disulphide [$(H_4N)_2S_2$] is prepared by passing sulphur vapor and ammonia gas through a red-hot porcelain tube. The crystals are yellow and transparent.

Boyle's fuming liquor, prepared by distilling sal-ammoniac with lime and sulphur, is the *hydrated diammonic sulphide*. Its solution in water, which dissolves sulphur freely, forms an **Ammonic Pentasulphide** [$(H_4N)_2S_5$], from which solution the sulphur may be obtained in oblique rhombic prisms. A sulphide with the formula [$(H_4N)_2S_7$] has been obtained. It is a red crystalline body.

(9.) **Ammonic-hydric Sulphide**, *Hydrosulphate of ammonia* (NH_4HS).

Preparation.—(1.) (*As a solution.*) By saturating a solution of ammonia with sulphuretted hydrogen.

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(2.) In the *anhydrous* form by mixing two volumes of ammonia with two of sulphuretted hydrogen.

Properties.—The anhydrous salt is colorless, transparent, very volatile, subliming unchanged, and soluble in water.

The solution is at first colorless, but speedily becomes yellow by absorbing oxygen, whereby ammonic disulphide and ammonic thiosulphate (hyposulphite) are formed.—

$$8H_4NHS + 5O_2 = 2[(H_4N)_2S_2] + 2[(H_4N)_2S_2O_3] + 4H_2O.$$

Finally sulphur is deposited, the solution then containing ammonic hyposulphite, sulphite and sulphate.

The solution is largely used in the laboratory as a test reagent. Two important facts should be remembered :—

I. On the addition of *an acid*,—(*α.*) *the fresh solution* gives off H_2S, the solution itself remaining *clear* :—

$$NH_4HS + HCl = NH_4Cl + H_2S.$$

(*β.*) *Whilst the old solution* also gives off H_2S, but the solution becomes *turbid* from the deposition of sulphur by the action of the acid on the diammonic disulphide :—

$$(NH_4)_2S_2 + 2HCl = 2NH_4Cl + H_2S + S.$$

II. With *acetate of lead.*—(*α.*) *The fresh solution* gives a *black* precipitate of plumbic sulphide (PbS).

(*β.*) The *old solution* gives a *red* precipitate of plumbic persulphide.

(10.) Ammonic Sulphate $[(H_4N)_2SO_4]$. — *Preparation.* By distilling gas liquor with lime, and condensing the ammonia in sulphuric acid. It is found native as mascagnine, and is also found on the windows and furniture of rooms where gas is burnt.

Properties.—A crystalline salt, soluble in water (1 in 2 aq.). When heated the crystals first decrepitate, then melt (284° F. or 140° C), and finally decompose (500° F. or 260° C.), ammonic sulphate being formed together with H_2O, NH_3, N, and SO_2.

It is used as a manure, and also to render muslin non-inflammable.

An acid or **Hydric Ammonic Sulphate** $(H_4N)_3H2SO_4$, and a **Sodic Ammonic Sulphate** $(H_4N)NaSO_4,2H_2O$ are also known.

(13-15.) Normal Ammonic Carbonate $[(H_4N)_2CO_3]$ is not known, but probably exists in solution.

Ammonic Sesquicarbonate or *common carbonate of ammonia* or *Preston smelling salts* $[2(H_4N)_2O,3CO_2]$ is prepared by heating a mixture of chalk and ammonic chloride (or sulphate). The sesquicarbonate formed is collected in a leaden vessel and afterwards purified by sublimation.

$$\underset{\text{Ammonic chloride}}{6H_4NCl} + \underset{\text{Calcic carbonate}}{3CaCO_3} = \underset{\text{Calcic chloride}}{3CaCl_2} + \underset{\text{Ammonia}}{2H_3N} + \underset{\text{Water}}{H_2O} + \underset{\text{Ammonic sesquicarbonate.}}{2[(H_4N)_2O,3CO_2]}.$$

The salt smells strongly of ammonia, and is soluble in cold water (1 in 3 aq.).

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On exposure to air the transparent sesquicarbonate gives off NH_3 and CO_2, and becomes opaque and crumbly, an *ammonic bicarbonate* being formed.

$$2(H_4N)_2O,3CO_2 = 2NH_3 + CO_2 + 2(H_4NHCO_3)$$

Ammonic sesquicarbonate = Ammonia + Carbonic acid + Ammonic bicarbonate.

The bicarbonate is also formed by the action of boiling water on the sesquicarbonate, or by acting with cold water on the sesquicarbonate. In this latter case a solution of the normal carbonate is obtained, and the bicarbonate, a more sparingly soluble salt (1 in 8 aq.) left.

16.—Ammonic Nitrate (H_4NNO_3) is prepared by neutralising ammonic sesquicarbonate with nitric acid. It is a crystalline, deliquescent salt, soluble in water with the production of great cold. On the application of heat it first melts (226 F°. or 107·8° C.), and then decomposes (at 482° F. or 250° C.), into water and nitrous oxide, and at a greater heat into water, nitric oxide and nitrogen.

17.—Microcosmic Salt or **Sodic Ammonic Hydric Phosphate** ($Na,H_4N,H,PO_4,4H_2O$) is the only ammonic phosphate of importance, although phosphates of ammonia corresponding to the sodic phosphates are known.

Preparation.—By acting on a solution of 1 part of ammonic chloride with 6 parts of hydric disodic phosphate, sodic chloride being also formed. The microcosmic salt is purified from the solution by successive recrystallizations.

Properties.—It is very soluble. By heat the ammonia and water are driven off, a sodic metaphosphate remaining. This compound becomes a colorless glass at a red heat, and in this state dissolves various metallic oxides, forming with them beads of different colors. Hence its use in blow-pipe experiments.

Tests for Ammonium Compounds.—(*See* ANALYTICAL TABLES.)

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CHAPTER XIII.

GROUP V.—THE METALS OF THE ALKALINE EARTHS.

BARIUM and its Compounds—STRONTIUM and its Compounds—CALCIUM and its Compounds—MAGNESIUM and its Compounds.

Metal.	Symbol.	Atomic Weight.	Atomic Volume.	Specific Gravity.	Electric Conductivity 68°—62° F.
Barium	Ba	137·0	34·25	4·00	..
Strontium	Sr	87·6	34·49	2·54	6·71
Calcium	Ca	40·0	25·35	1·57	22·14
Magnesium ..	Mg	24·0	13·77	1·74	25·47

Barium, strontium and calcium are distinguished from the members of Group I., as follows:—

(1.) They are divalent elements.

(2.) They are heavier than water.

(3.) They decompose water less energetically.

(4.) Their oxides and sulphides are less soluble in water.

(5.) Their carbonates are insoluble in pure water, but are soluble in water containing CO_2.

(6.) Their sulphates, phosphates and oxalates are either entirely or nearly insoluble.

Further note:—

(1.) They each form two oxides, of which one is basic and forms a hydrate with water of the formula $M''H_2O_2$.

(2.) They each form one chloride $M''Cl_2$

We class magnesium with the metals of the alkaline earths for convenience, although its power of resisting oxidation at ordinary temperatures, its volatility at high temperatures, the sparing solubility of its oxide and sulphide, and the solubility of its sulphate, more nearly ally it to zinc and cadmium.

BARIUM ($Ba''=137.$)

Atomic and molecular weight 137. *Specific gravity* 4·0. *Fuses below a red heat. Atomicity, dyad* ($Ba''Cl_2$)

History.—Discovered by Sir H. Davy.

Natural History.—Found as *heavy spar* ($BaSO_4$) and *Witherite* ($BaCO_3$).

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Preparation.—(1.) By electrolysing baric chloride, using mercury for the negative pole, whereby an amalgam with barium is produced, from which the mercury may be afterwards expelled by heat.

(2.) An amalgam of barium may also be formed by the action of a sodium amalgam on a solution of baric chloride.

(3.) By passing the vapour of potassium over red hot baric oxide or chloride.

Properties.—A pale yellow, malleable metal, melting below a red heat, quickly tarnishing in air, decomposing water at ordinary temperatures ($Ba + 2H_2O = H_2 + BaH_2O_2$), and glass at a red heat.

All the barium compounds are soluble, colorless (if the acid be colorless) and poisonous. Sodic or magnesic sulphates are the proper antidotes.

Compounds of Barium.

	Names.	Formula (common.)	Formula (constitutional.)	Molecular weight of anhydrous salt.	Specific gravity of crystals.	BaO or = to BaO in 100 parts.
1	Baric oxide (baryta)	Ba″O	**Ba**″O	153	5·456	100·00
2	,, dioxide (peroxide of barium)	BaO_2	**Ba**$\begin{matrix}O\\O\end{matrix}$	169		90·53
3	Baric hydrate ..	BaH_2O_2	**Ba**H_2O_2	171	4·495	89·47
4	,, chloride ..	$BaCl_2,2H_2O$	**Ba**Cl_2,2OH_2	208	3·052	73·55
5	,, sulphide ..	BaS	**Ba**S	169		90·53
6	,, disulphide ..	BaS_2	**Ba**$\begin{matrix}S\\S\end{matrix}$	201		76·11
7	,, sulphate ..	$BaSO_4$	**S**O_2Bao″	233	4·59	65·66
8	,, nitrate ..	Ba2NO_3	**N**O_2Bao″ **N**O_2Bao″	261	3·284	58·62
9	,, carbonate ..	$BaCO_3$	**C**OBao″	197	4·3	77·67
10	,, chlorate ..	$Ba(ClO_3)_2$	OCl O Bao″ O OCl	304		50·32

Compounds of Barium with Oxygen and Hydroxyl.

Baric oxide—BaO.
Baric peroxide—BaO_2.
Baric hydrate—BaH_2O_2.

(1.) Baric oxide, *Baryta* (BaO), is the residue left on igniting baric nitrate. It freely absorbs moisture and carbonic anhydride, and slakes with water, forming baric hydrate.

(2.) Baric Peroxide, or *Dioxide* (BaO_2) is prepared by heating baric oxide in a current of oxygen, or with potassic chlorate. It is used in the preparation of hydroxyl. When heated it gives off oxygen, leaving BaO.

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(3.) **Baric Hydrate,** *Caustic baryta* (BaH_2O_2). *Preparation.* (1.) By the action of water on baryta (BaO). (2.) By boiling baric sulphide with cupric oxide ($BaS + CuO + OH_2 = BaHo_2 + CuS$).

Properties.—It rapidly absorbs CO_2. It is not decomposed by heat. It is soluble in water (1 in 20 at 60° F., and 1 in 3 at 212° F.), but is almost insoluble in alcohol.

(4.) **Baric Chloride** ($BaCl_2 2H_2O$) is prepared by dissolving $BaCO_3$ in HCl. It crystallises in flat prisms, which are soluble in pure water (1 in 2 at 60° F.), but are much less soluble if the water contains any free acid.

Barium Oxysalts.

(7.) **Baric Sulphate** ($BaSO_4$) is found native. It is insoluble in water, and in all acids except in boiling sulphuric acid. It is used by artists as a paint (*permanent white*), and is employed as an adulterant of white lead. Heated with carbon, it, in common with all sulphates, becomes a sulphide.

(8.) **Baric Nitrate** ($Ba2NO_3$) is prepared by the action of HNO_3 on $BaCO_3$. The crystals are octahedral, insoluble in alcohol, but soluble in water (1 in 8 at 60° F., and 1 in 3 at 212° F.). When heated it melts, leaving finally baric oxide ($2BaN_2O_6 = 2BaO + 2N_2O_4 + O_2$). It is used for pyrotechny.

(9.) **Baric Carbonate,** *Witherite* ($BaCO_3$), is prepared by the action of an alkaline carbonate on a barium salt. It is *insoluble* in water containing saline matter, *almost insoluble* in pure water, but *soluble* in water containing CO_2.

Tests for Barium Compounds.—(*See* Analytical Table.)

STRONTIUM ($Sr'' = 87{\cdot}5$).

Atomic and Molecular weight, 87·5; *Specific gravity,* 2·54; *Atomicity dyad* ($Sr''Cl_2$).

History.—Discovered by Sir H. Davy in 1808.

Natural History.—Found as *strontianite* ($SrCO_3$) and as *celestine* ($SrSO_4$).

Preparation.—Similar to the preparation of barium (see page 315).

Properties.—A white, or according to Matthiessen a dark yellow metal, malleable, burning in air with a crimson flame, and decomposing water at common temperatures, with the evolution of hydrogen. It is soluble in dilute but not in concentrated nitric acid.

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Compounds of Strontium.

	Names.	Formula (common.)	Formula (constitutional.)	Atomic weight of anhydrous salt.	Specific Gravity of crystals.	SrO in 100 parts.
1	Strontic oxide (strontia)	SrO	SrO	103·6	4·611	100·0
2	,, peroxide ..	SrO_2	$Sr\begin{matrix}O\\O\end{matrix}\}$	119·6		86·62
3	,, hydrate	$SrH_2O_2,2H_2O$	$SrHo_2,8OH_2$	121·6	1·396	85·19
4	,, chloride	$SrCl_2,3H_2O$	$SrCl_2,3OH_2$	158·6	1·603	65·32
5	,, sulphate.. ..	$SrSO_4$	SO_2Sro''	183·6	3·9	56·43
6	,, nitrate	$Sr2NO_3$	$\{\begin{matrix}NO_2\\NO_2\end{matrix}\}Sro''$	211·6	2·305	
7	,, carbonate ..	$SrCO_3$	$COSro''$	147·6	3·65	70·19

(1.) Strontic Oxide.—*Strontia* (SrO). Corresponds in all respects to BaO (see page 315).

(2.) Strontic Peroxide (SrO_2).

Preparation.—By the action of hydroxyl on strontic hydrate ($SrH_2O_2+H_2O_2=SrO_2+2H_2O$).

All the strontic salts are white if the acid with which the metal is combined be colorless.

Tests for Strontium Compounds.

1. Strontium compounds color the blowpipe flame red.

2. In the spectrum several bright bands are seen in the red and orange, and a brilliant band in the blue.

3. Tests similar to barium compounds, excepting that

4. *Silico-fluoric acid* and *sodic thiosulphate* give no precipitate with strontium salts. Strontic silico-fluoride (SrF_2,SiF_4), unlike the barium compound, is soluble in water.

For further Tests *see* ANALYTICAL TABLES.

CALCIUM (Ca″=40).

Atomic weight, 40; *Specific gravity*, 1·578; *Atomicity, dyad* ($CaCl_2$).

History.—Discovered by Sir Humphry Davy, 1808.

Natural History.—Found (α.) in the *mineral* kingdom, as marble, limestone, calcspar, etc. ($CaCO_3$); and as gypsum, selenite, alabaster, etc. ($CaSO_4$); as a *fluoride* in fluorspar; as a *phosphate* in apatite, phosphorite, etc.

(β.) In the *animal* kingdom it is found in bones as a phosphate, and in eggshells, oystershells, etc., as a carbonate.

(γ.) It is present in all *vegetables*.

Preparation.—(1.) By processes similar to those described for the preparation of barium and strontium (see page 315).

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(2.) By igniting sodium with calcic iodide.

(3.) By heating an alloy of zinc and calcium (formed by fusing together zinc, sodium, and calcic chloride) so as to volatilise the zinc.

Properties.—A light yellow, very hard, malleable, ductile metal. It melts at a red heat, tarnishes in air, and decomposes water. It is rapidly acted on by dilute acids, and burns when heated with a brilliant white light.

Compounds of Calcium.

	Names.	Formula (common).	Formula (constitutional).	Atomic Weight of Anhydrous Salt.	Specific Gravity of the Crystal.	Ca or CaO in 100 parts.
1	Calcic oxide (quick lime)	CaO	$\mathbf{C}aO$	56	3·18	Ca=71·43
2	Calcic peroxide ..	CaO_2	$\left\{ \begin{matrix} O \\ \mathbf{O} \end{matrix} \right.Ca$			
3	Calcic hydrate—(slaked lime) ..	CaH_2O_2	$\mathbf{C}aHo_2$	74	2·078	CaO=75·68
4	Calcic chloride ..	$CaCl_2$	$\mathbf{C}aCl_2$	111	Crystallized 1·680 Fused .. 2·485	Ca=36·03
5	,, bromide ..	$CaBr_2$	$\mathbf{C}aBr_2$			
6	,, iodide ..	CaI_2	$\mathbf{C}aI_2$			
7	Calcic fluoride—(fluor spar) ..	CaF_2	$\mathbf{C}aF_2$	78	3·4	Ca=51·28
8	Calcic sulphide ..	CaS	$\mathbf{C}aS$	72		
9	Calcic disulphide..	CaS_2	$\left\{ \begin{matrix} S \\ \mathbf{S} \end{matrix} \right.Ca$			
10	Calcic pentasulphide	CaS_5	$\mathbf{C}aS_5$			
11	Calcic thiosulphate (hyposulphite).	CaS_2O_3	$\mathbf{S}S''OCao''$			
12	Calcic hypochlorite	$CaCl_2O_2$	$\mathbf{C}a(OCl)Cl$			
13	Calcic phosphide ..	$Ca_2P_2(?)$	..	142		
14	Calcic sulphate—(gypsum) ..	$CaSO_4$	$\mathbf{S}O_2Cao''$	136	Crystallized 2·30 Anhydrous 2·95	CaO=41·18
15	Calcic nitrate ..	$Ca2NO_3,4H_2O$	$\left\{ \begin{matrix} \mathbf{N}O_2 \\ \mathbf{N}O_2 \end{matrix} \right.Cao'',4OH_2$	164	Crystallized 1·780 Anhydrous 2·24	
16	Calcic carbonate—(chalk)	$CaCO_3$	$\mathbf{C}OCao''$	100	2·72	CaO=56·00
17	Tricalcic phosphate (bone earth) ..	$Ca_3P_2O_8$	$\mathbf{P}_2O_2Cao''_3$			
18	Calcic phosphate (superphosphate)	$Ca''H_42PO_4$	$\mathbf{P}_2O_2Ho_4Cao''$			
19	Calcic disilicide ..	Si_2Ca				
20	Calcic oxalate ..	$CaC_2O_4,2H_2O$	$\left\{ \begin{matrix} \mathbf{C}O \\ \mathbf{C}O \end{matrix} \right.Cao'',2OH_2$	128		

Compounds of Calcium with Oxygen and Hydroxyl.

Calcic oxide ... ... CaO.
Calcic peroxide ... ... CaO_2.
Calcic hydrate ... ... CaH_2O_2.

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(1.) Calcic Oxide; *Lime, Quicklime* (CaO). *Preparation.*—(1.) By heating together coal and limestone ($CaCO_3$); (2.) Pure CaO may be prepared by heating Carrara marble to redness for some hours in an open fire.

Properties.—A white, caustic, infusible substance, combining rapidly with water (*slaking*), by which process great heat is evolved. The lime swells up during the process (*live-lime*), and finally crumbles to a white powder, forming CaO,H_2O, called *slaked lime* or *solid calcic hydrate.* When exposed to the air, lime absorbs both moisture and carbonic anhydride, becoming what is called "*air-slaked*" lime, a compound represented by the formula ($CaCO_3$,CaH_2O_2).

(2.) Calcic Peroxide (CaO_2) is prepared like SrO_2 (see page 317.)

(3.) Calcic Hydrate, *Slaked lime* (CaH_2O_2), is prepared by the action of water on quick lime (CaO). When heated to a red heat, H_2O is expelled, and CaO remains.

A white creamy mass called "*milk of lime*" is produced when calcic hydrate is diffused in water. Calcic hydrate is twice as soluble in cold (1 in 700 or 0·5 gr. to ℥j.) as it is in hot water, the solution being known as "*lime-water*," which is an alkaline liquid, rapidly absorbing CO_2 from the air. By evaporating lime-water "in vacuo" a crystalline hydrate (CaH_2O_2) may be obtained (Gay Lussac).

Uses of Lime.

Mortar, *which is used for buildings exposed to the action of air only,* consists of lime and sand, the latter being added, as in the case of pottery, to increase the cohesive power of the lime, and to prevent its shrinking as it dries. Before the mortar is applied, the bricks are wetted, in order to prevent their absorbing moisture too rapidly from the mortar. It is not very clear why mortar dries. The surface, and the surface only of the mortar becomes carbonated, whilst to a certain extent combination takes place between the lime and the silica, forming a calcic silicate.

Mortar, when exposed to the action of water, disintegrates. Hence it cannot be used for sub-aqueous constructions.

Cements, or Hydraulic Mortars *are employed for buildings exposed to the action of water.* They consist of a calcined mixture of carbonate of lime and clay (10 to 30 per cent.), whereby calcic silicate and some aluminic silicates (the silica being derived from the clay or lime) are formed. The powdered calcined mass, when mixed with water, solidifies, owing to the formation of hydrated double silicates and aluminates, a substance being thus formed of great hardness, and upon which water has no action.

The rapidity of solidification depends on the quantity of clay present. If it contains 25 to 35 per cent., it hardens in a few hours, and constitutes what is called *Roman cement*, a substance commonly

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manufactured from the nodules of calcareo-argillaceous ironstone, found in the London clay.

Portland cement consists of a calcined mixture of lime and mud (clay) taken from the river Medway. The mass, when dry, has the appearance of Portland stone.

Concrete is a mixture of hydraulic cement with gravel or coarsely powdered pebbles. *Scott's cement* is lime, containing a small proportion of calcic sulphate.

Lime is also used as a manure, for the purification of coal gas, and for various other purposes.

(4.) **Calcic Chloride** ($CaCl_2$).—*Preparation.* (1.) By the action of HCl on $CaCO_3$. The solution is evaporated to dryness, when $CaCl_2,6H_2O$ is obtained, which, at 390° F., becomes $CaCl_2,2H_2O$, and above this heat $CaCl_2$. (2.) It is also obtained, as a secondary product, in the manufacture of ammonic carbonate (*see* page 312). Thus—

$$6H_4NCl + 3CaCO_3 = 3CaCl_2 + 2[(H_4N)_2O,3CO_2] + 2H_3N + H_2O.$$

Properties.—A white, very deliquescent salt, soluble in alcohol and in water, the saturated aqueous solution boiling at 355° F. (179·5° C.). It absorbs ammonia freely.

Uses.—It is used in the laboratory in the solid form as a dessicant, and its solution is employed as a bath to obtain a steady, continuous temperature. The crystals mixed with ice form a powerful freezing mixture.

(7.) **Calcic Fluoride**, *Fluor spar* (CaF_2) is found as a mineral in sea and in other water, and also in the bones and teeth of animals. It is the source of all the fluorine compounds.

(8.) The **Calcic Sulphides** are mostly soluble. CaS forms one of the principal constituents of the "*soda waste*" of the alkali works. By exposure to air, it becomes calcic thiosulphate (hyposulphite), ($2CaS + H_2O + 2O_2 = CaH_2O_2 + CaS_2O_3$), and by the action of sodic carbonate is converted into sodic thiosulphate (*see* page 272).

(14.) **Calcic Sulphate** ($CaSO_4$) is found in nature as *anhydrite* ($CaSO_4$), and as *gypsum, alabaster, selenite,* etc., ($CaSO_4,2H_2O$); also in various waters (selenitic), constituting one source of *permanent hardness.*

Properties.—It occurs in flattened prisms (selenite) and in earthy masses (gypsum). It is soluble in water (1 in 500=140 grs. per gallon at 60° F.), its solubility being diminished by the presence of calcic and magnesic chlorides. It is insoluble in alcohol and in dilute nitric and hydrochloric acids.

Uses.—*Plaster of Paris* consists of finely-powdered gypsum calcined at 500° F. (260° C.), so as to drive off the two molecules of water it contains. When the calcined mass is mixed with water it rapidly solidifies and expands, again combining with the two molecules of water expelled by the previous heat. If "overburnt" this property of recombination with water is destroyed. By exposure to air,

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plaster of Paris deteriorates, owing to its absorbing moisture. *Stucco* is plaster of Paris mixed with a solution of size, whilst various cements are formed by its admixture with a solution of alum, borax, etc., by which means the hardness of the mass, when set, is greatly increased. *Scagliola*, or *artificial marbles*, are formed by the insertion into the stucco of pieces of natural stone.

The "*pearl hardener*" of the paper-makers is freshly precipitated calcic sulphate.

(15.) **Calcic Nitrate** ($Ca2NO_3,4H_2O$) is a crystalline deliquescent salt, soluble in alcohol.

(16.) **Calcic Carbonate** ($CaCO_3$) is found native, both in an uncrystallized state, as limestone, chalk, oolite, etc., and also in minute granular crystals (as marble), either colored with iron or manganese oxides, or of a black tint, due to the presence of bituminous matter. It also occurs in large six-sided crystals, as arragonite, and in rhombohedral crystals, as Iceland or calc spar, etc.

In the *animal* kingdom it forms the chief constituent of corals, of fish, and of egg-shells; and it enters largely into the formation of bones. Pearls are also composed of it.

Properties.—A white, crystalline (dimorphous) body, almost insoluble in pure water (2 grs. in 1 gallon), but soluble in water containing carbonic anhydride, from which solution it is deposited when the gas is driven off. In this way the stalactites and stalagmites of Derbyshire are formed, and also the tufa and travertine of volcanic districts. It is decomposed by heating in air ($CaCO_3=CaO+CO_2$), and also by the action of HCl,HNO_3 or H_2SO_4.

It constitutes one and the chief cause of the *temporary hardness* of water, that is, hardness removable by boiling (*see* p. 208). The deposition of the lime and magnesic carbonates in boilers, constitutes what is called "furring," and renders a water containing an excess unsuitable for boiler purposes. The deposition, however, may be, in a great measure, prevented by the addition to the water of a little soda ash or ammonic chloride. In the latter case, ammonic carbonate is formed, which volatilises along with the steam, a soluble calcic chloride remaining. Dr. Clark has suggested a plan of softening hard waters by adding a sufficiency of lime to combine with the carbonic acid holding the carbonate of lime in solution, whereby the calcic carbonate pre-existent in the water and that formed by the union of the carbonic acid and the additional lime, are precipitated together.

Calcic carbonate constitutes the basis of many building materials, such as marble, Portland stone, Bath stone, magnesian limestone, of which the Houses of Parliament are built. The decay of such stones is dependent, in a town, on the action of sulphuric acid (produced by burning coal), and of carbonic acid, as well as by mechanical disintegration occasioned by the expansion of the water in the pores of the stone in the act of freezing.

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(17-18.) Calcic Phosphates.—The *Tricalcic phosphate* ($Ca_3P_2O_8$) occurs native in *osteolite, coprolite,* etc. It is the principal ingredient of bone-ash. Various calcic phosphates known as *phosphorite, apatite,* etc., are also found native. *Calcic superphosphate* ($Ca''H_4,2PO_4$) is formed by treating bone-earth with oil of vitriol.

(20.) Calcic Oxalate ($CaC_2O_4,2H_2O$) is a white insoluble body, precipitated when ammonic oxalate is added to a lime solution. It is insoluble in acetic acid, but is converted by heat into calcic carbonate ($CaC_2O_4=CaCO_3+CO$).

Chloride of Lime, or "*Bleaching powder,*" is prepared by passing chlorine over slaked lime. The lime absorbs nearly half its weight of chlorine. Formerly the compound was regarded as a mixture of calcic chloride and hypochlorite. Thus—

$$2CaH_2O_2 + 2Cl_2 = \underbrace{CaCl_2 + CaCl_2O_2}_{\text{Bleaching powder.}} + 2H_2O.$$

Calcic hydrate + Chlorine = Bleaching powder. + Water.

But inasmuch as bleaching powder is *not deliquescent* (when well made) and *not soluble in alcohol* as calcic chloride is, this compound is now believed to be a definite chemical combination, viz., a calcic-chloro-hypochlorite, Ca(OCl)Cl.

It is decomposed by water, by heat, by moist air (hypochlorous acid being evolved), and by acids.

Tests for Lime and its compounds.—(*See* ANALYTICAL TABLES.)

MAGNESIUM (Mg'').

(*Atomic and molecular weight,* 24. *Specific gravity,* 1·743. *Atomicity, dyad.* ($MgCl_2$). *Fuses at a red heat*). Its general properties, the volatility of its chloride, the solubility of its sulphate, and the isomorphism of its compounds with those of zinc, ally it, so far as its general chemistry is concerned, to this metal, rather than to the metals of the earths.

We consider it here for convenience.

History.—Prepared by Davy in 1808, and studied by Bussy in 1830.

Natural History.—It occurs (α) in the *mineral* kingdom as magnesite ($MgCO_3$), dolomite or magnesian limestone ($Ca''Mg''2CO_3$), as brucite (MgH_2O_2), and as boracite, hydroboracite, and pearl spar. As a *silicate* it is found in the form of mica, asbestos, hornblende, serpentine, olivine, steatite (soapstone or French chalk), meerschaum, talc, etc. It occurs in most waters as a carbonate and a sulphate. (β.) It is found in *animals* and *vegetables* in combination with carbonic, phosphoric, and most organic acids.

Preparation.—(1.) By the electrolysis of fused magnesic chloride. (Davy.)

(2.) By heating a mixture of metallic potassium and magnesic chloride. (Bussy.)

(3.) By fusing a mixture of $MgCl_2$,NaCl,CaF_2 and Na.

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Properties.—(*a.*) *Physical.* A white, hard, light, malleable, ductile metal, melting at a red heat, and sufficiently volatile that if heated in a hydrogen atmosphere it may be distilled. It is insoluble in cold water, but is soluble in acidulated water and in ammonic chloride ($4NH_4Cl + Mg = 2NH_4Cl, MgCl_2 + H_2 + 2NH_3$).

(*β.*) *Chemical.* It decomposes warm but not cold water. It is not easily affected by *dry* air, but is rapidly oxidized in *moist* air at ordinary temperatures. It burns in air (forming $(MgO)_2$, the light evolved being of great intensity, and highly actinic. It also burns in chlorine, bromine, iodine, and in sulphur vapors. It combines, with nitrogen at high temperatures to form a nitride (N_2Mg_3). It ignites when placed in HCl, but is not acted on by cold nitro-sulphuric acid. It reduces acid solutions of salts of many of the metals, hydrogen gas, or, as in the case of arsenical and antimonial compounds, arseniuretted or antimoniuretted hydrogen, being evolved.

Uses.—It is used as a source of light in photography, the magnesium spectrum being continuous and of high actinism.

Compounds of Magnesium.

SALTS.	Ordinary Formula.	Constitutional Formula.	Molecular Wt. of Anhydrous Compound.	Specific Gravity of Crystals.	Anhydrous Salt contains Mg or MgO per cent.
1 Magnesic oxide (magnesia) ..	MgO	$\mathbf{Mg}O$	40	3·6	Mg=60
2 Magnesic hydrate	MgH_2O_2	$\mathbf{Mg}Ho_2$			
3 „ chloride	$MgCl_2$	$\mathbf{Mg}Cl_2$	95	with $6H_2O$ 1·562 anhydrous 2·177	
4 „ bromide	$MgBr_2$	$\mathbf{Mg}Br_2$	184		
5 „ nitride	Mg_3N_2				
6 „ sulphide	MgS	$\mathbf{Mg}S$	56		
7 „ sulphate (Epsom salts) ..	$MgSO_4,7H_2O$	$SOHo_2Mgo'',6OH_2$	120	Crystals 1·660 Anhydrous 2·706	MgO=16·26 MgO=33·33
8 Magnesic nitrate	$Mg2NO_3,6H_2O$	$\mathbf{NO_2}Mgo'',6OH_2$	148	1·464	
9 „ carbonate (basic carbonate)	$MgCO_3$ $MgCO_3,MgH_2O_2,3H_2O$	$\mathbf{NO_2}$ $\mathbf{C}OMgo''$	84	3·056	
10 Hydric magnesic phosphate ..	$H_2Mg_2''2PO_4,14H_2O$				
11 Ammonic magnesic phosphate (triple phosphate) ..	$Mg''_2(H_4N)_2 2PO_4,12H_2O$		274		
12 Magnesic pyrophosphate ..	$Mg_2P_2O_7$	$P_2O_3Mgo''_2$			
13 Magnesic phosphate	$Mg_3P_2O_8$	$P_2O_2Mgo''_3$			
14 Magnesic borate ..	$3MgO,4B_2O_3$	$B_8O_9Mgo''_3$			
15 „ silicates (various)					

(1.) Magnesic Oxide, *Magnesia* (MgO). This is the only oxide of magnesium.

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Preparation.—It may be prepared by burning magnesium in air, or by igniting magnesic carbonate or nitrate in a crucible. It is a white and almost insoluble powder. Like lime, baryta, and strontia, it slakes with water; but, unlike them, it develops no heat in doing so. The magnesic hydrate (MgH_2O_2) thus formed, slowly absorbs atmospheric carbonic anhydride. The hydrate forms a compact mass like plaster of Paris, and may be used for casts. Magnesic oxide, when placed on turmeric paper and moistened, turns the paper brown.

(2.) **Magnesic Hydrate** (MgH_2O_2) occurs in nature as brucite, and may be prepared, in addition to the above method, by precipitating magnesic sulphate with potassic hydrate ($MgSO_4+2KHO=K_2SO_4+MgH_2O_2$). It is insoluble in water, and infusible by heat.

(3.) **Magnesic Chloride** ($MgCl_2$) is found in sea water. It may be prepared by acting on magnesia or magnesic carbonate with hydrochloric acid. On evaporation to dryness, the $MgCl_2$ is decomposed ($MgCl_2+H_2O=2HCl+MgO$). If ammonic chloride, however, be added to the solution before it is evaporated, the double salt ($MgCl_2,2NH_4Cl$) is formed, from which the NH_4Cl may be volatilized, leaving pure $MgCl_2$ in a fused state.

It is a crystalline deliquescent substance, freely soluble in water and in alcohol.

(4.) **Magnesic Bromide** ($MgBr_2$) is found in sea water and in saline springs.

(5.) **Magnesic Nitride** (Mg_3N_2) may be produced by the direct union of nitrogen and magnesium. It is a crystalline body, easily decomposed by water ($N_2Mg_3+3H_2O=2NH_3+3MgO$).

(6.) **Magnesic Sulphide** (MgS) is slightly soluble in water.

(7.) **Magnesic Sulphate,** *Epsom salts* ($MgSO_47H_2O$), is found native in small quantities in most waters, but in great abundance in certain springs in the neighbourhood of Epsom.

Preparation.—By calcining dolomite ($MgCa2CO_3$), a mixture is formed of MgO and CaO. This residue, after being washed to extract some of the lime, is acted on with sulphuric acid, whereby $MgSO_4$ and $CaSO_4$ are formed, the latter of which, being insoluble, is precipitated. The magnesic sulphate may then be obtained from the clear solution by evaporation.

It may also be prepared from the "bittern" of sea water (that is, the liquor remaining after the extraction of the common salt), as well as from the liquor of the alum works.

Properties.—A white crystalline (right rhombic prisms), bitter tasted, slightly efflorescent salt. It is soluble in water (1 in 3 aq. at 60° F., and 1 in 1·5 aq. at 212° F.). By a heat of 212° F. (100° C.), six of its water molecules may be driven off, whilst the seventh molecule needs a very much higher temperature to effect its separation. This seventh molecule may be displaced by a molecule of an anhydrous salt (such as K_2SO_4), a double salt being formed (such as

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$MgSO_4,K_2SO_4,6H_2O$), having the same crystalline form as magnesic sulphate.

(9.) **Magnesic Carbonate** ($MgCO_3$). — *Natural History.* Found native as magnesite and (together with $CaCO_3$) as dolomite.

Preparation.—Boiling solutions of K_2CO_3 and $MgCl_2$ are mixed together, and the precipitate formed dissolved in carbonic acid water. From this solution the salt is deposited ($MgCO_3,3H_2O$) as the carbonic anhydride escapes. "Magnesia alba" ($MgCO_3,H_2O,MgH_2O_2$) is prepared by precipitating a magnesic sulphate solution with a sodic carbonate solution.

(11.) **Ammonic Magnesic Phosphate,** *Triple phosphate;* ($Mg_2(H_4N)_22PO_4,12H_2O$) is an important salt, magnesia being usually precipitated in analysis in this form. It is insoluble in water containing free ammonia. On igniting the salt, magnesic pyrophosphate ($Mg_2P_2O_7$) is formed, from which the quantity of magnesia may be estimated.

Triple phosphate is a frequent constituent of urinary calculi.

(15.) The **Magnesic Silicates** are numerous. Talc ($4MgO,5SiO_2$), steatite ($3MgO,4SiO_2$), meerschaum ($2MgO,3SiO_2,4H_2O$), and serpentine ($2[(MgFe)O,SiO_2]MgO,2H_2O$) are a few illustrations of its more common forms.

Tests.—(*See* ANALYTICAL TABLES.)

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CHAPTER XIV.

THE METALS OF GROUP IV.

MANGANESE and its Compounds — ZINC and its Compounds — COBALT and its Compounds—NICKEL and its Compounds—URANIUM and its Compounds—INDIUM and its Compounds.

MANGANESE (Mn=55).

Specific gravity 7·0 *to* 8·1. *Atomicity, dyad, tetrad, and hexad, also a pseudo-triad and an octad; a dyad as in Manganous compounds* (MnO; $MnSO_4$), *and a tetrad* (*although apparently a triad*) *in Manganic compounds* (Mn_2O_3; Mn_2Cl_6).

History.—Manganese was used in early times, although its nature was not understood, to color glass. The oxide was recognised by Scheele in 1774, and the metal obtained by Gahn in 1780.

Natural History.—Manganese is not found in a free state. It occurs as an *oxide* in hausmannite, Mn_3O_4, braunite, Mn_2O_3, and pyrolusite, MnO_2; as a *sulphide* in manganese blende, MnS; as a *carbonate* in manganese spar, $MnCO_3$; and as a *silicate* in red manganese, $MnSiO_3$. It is found in the ashes of plants.

Preparation.—(1.) By reducing manganous carbonate with charcoal.

(2.) By the electrolysis of manganous chloride.

(3.) By the action of sodium on manganic fluoride.

(4.) By reducing the oxide with carbon in a crucible of caustic lime. (Deville.)

Properties.—(α.) *Physical.* A greyish-white or reddish metal, brittle, but so extremely hard that it will scratch steel. It is feebly magnetic, and very difficult to fuse.

(β.) *Chemical.* It is readily oxidized when exposed to the air. It decomposes water at ordinary temperatures, liberating hydrogen. It has a great attraction for carbon.

Uses.—It is mixed with iron for the purpose of hardening it.

COMPOUNDS OF MANGANESE AND OXYGEN.

MnO, Mn_2O_3, and MnO_2 exist in a free state; MnO_3 and Mn_2O_7 have never been isolated.

Chemically, it is to be noted that—

MnO is a powerful base.

Mn_2O_3 is feebly basic.

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$\left.\begin{matrix}Mn_3O_4\\MnO_2\end{matrix}\right\}$ are indifferent oxides, that is, are neither basic nor acid.

$\left.\begin{matrix}MnO_3\\Mn_3O_7\end{matrix}\right\}$ are anhydrides.

Compounds of Manganese.

		SALTS.	Ordinary Formula.	Constitutional Formula.	Molecular Weight, Anhydrous.	Specific Gravity.	Mn per cent.
1	Oxides.	Manganous oxide (protoxide)	$Mn''O$	**Mn**O	71		77·46
2		„ hydrate	MnH_2O_2	**Mn**Ho_2			61·79
3		Manganic oxide (sesquioxide)	$Mn'''_2O''_3$	**Mn**OMno″	158	4·82	69·62
4		„ red oxide	MnO,Mn_2O_3	$\left\{\begin{matrix}\textbf{Mn}O\\\textbf{Mn}O\end{matrix}\right\}$Mno″	229	4·72	72·05
5		Manganic dioxide (peroxide)	$Mn^{iv}O_2$	**Mn**O_2	87	4·94	63·22
6		Manganic anhydride	$Mn^{vi}O_3$ (?)	**Mn**O_3	103		53·39
7		Permanganic anhydride ..	$Mn^{vii}O_7$ (?)		222		
8	Chlorides.	Manganous chloride	$MnCl_2$	**Mn**Cl_2	126	2·01	43·65
9		Manganic chloride	$MnCl_4$	**Mn**Cl_4	197		27·91
10		Dimanganic hexachloride ..	Mn_2Cl_6	$\left\{\begin{matrix}\textbf{Mn}Cl_3\\\textbf{Mn}Cl_3\end{matrix}\right\}$	323		34·05
11		Manganous sulphate	$MnSO_4,7H_2O$	$SOHo_2$Mno″,$6OH_2$	151	3·1 of anhyd.	36·42
12		Manganous carbonate	$MnCO_3$	COMno″	115		47·82

(1.) **Manganous Oxide**, *Protoxide of Manganese* (MnO).

Preparation.—(1.) *Anhydrous.* By igniting manganous carbonate in a current of hydrogen.

(2.) As a *hydrate* (MnH_2O_2). By the addition of an alkali to a manganous salt.

Properties.—Manganous oxide has an olive-green color, and rapidly absorbs oxygen. The hydrate is white, but turns brown immediately on exposure to air. It is a powerful base. Its salts are flesh-colored.

(3.) **Manganic Oxide**, *Sesquioxide of Manganese* (Mn_2O_3).

Natural History.—Found native as *braunite* (Mn_2O_3), and as *manganite* (Mn_2O_3,H_2O).

Preparation (as a *hydrate*).—By first passing chlorine through water in which manganous carbonate ($MnCO_3$) is suspended, and subsequently removing the excess of carbonate with dilute nitric acid.

Properties.—A brown substance, decomposed by heat ($6Mn_2O_3 = 4Mn_3O_4 + O_2$). It colors glass violet (amethyst). It is a weak base, and isomorphous with alumina and ferric oxide. Thus in "manganese alum" manganic sulphate displaces aluminic sulphate—

$$\left(K_2SO_4 \left\{\begin{matrix}Mn_2 3SO_4\\\text{or}\\Al_2\ 3SO_4\end{matrix}\right. 24H_2O\right)$$

Its salts are red, and are decomposed by heat.

Action of Acids.—Strong sulphuric acid, when heated, decomposes

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it, liberating oxygen, and forming a manganous sulphate; dilute sulphuric acid dissolves it; nitric acid decomposes it into MnO and MnO_2, dissolving the former oxide; hydrochloric acid evolves chlorine when heated with it.

(4.) **Red Manganese Oxide** (Mn_3O_4) occurs native as "hausmannite," and may be prepared by heating any of the manganese oxides in the open air. It does not form salts. Fused borax and glass dissolve it, acquiring an amethyst color.

(5.) **Manganic Dioxide;** *binoxide, peroxide,* or *black oxide of manganese* (MnO_2).

Natural History.—Found native in a crystalline state as "pyrolusite, and in an amorphous form as "psilomelane." It occurs as a hydrate in "wad "and "varvicite" ($Mn_2O_3, 2MnO_2, H_2O$).

Preparation.—(1.) *Anhydrous.* By calcining the nitrate.

(2.) As a *hydrate.* (α.) By acting on potassic permanganate with an acid.

(β.) By heating Mn_3O_4 with nitric acid.

(γ.) By adding chloride of lime to a solution of a manganous salt.

Properties.—(α.) *Physical.* A black substance, insoluble in water. It is a good conductor of electricity. It is decomposed by heat ($3MnO_2 = Mn_3O_4 + O_2$).

(β.) *Chemical.* MnO_2 is an indifferent oxide, that is, it is neither acid nor basic. Heated with *sulphuric acid* oxygen is evolved, and a manganous sulphate formed ($2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$). With *hydrochloric acid* chlorine is set free, and a manganous chloride formed. *Nitric acid* is without action upon it. Manganic dioxide is largely used for the preparation of the chlorine required in the manufacture of bleaching-powder. Inasmuch as MnO_2 usually contains iron, the residual liquor also contains mixed manganous and ferric chlorides. From this liquor the manganous chloride may be again converted into oxide by adding a little lime to the mixed solution, which precipitates the *per*-chloride of iron without decomposing the protochloride of manganese, peroxides being weaker bases than protoxides ($Fe_2Cl_6 + 3CaO = Fe_2O_3 + 3CaCl_2$). The manganese may now be thrown down with chalk as a carbonate from the solution ($MnCl_2 + CaCO_3 = MnCO_3 + CaCl_2$), which is then roasted at 600° F., and the MnO_2 reproduced. (Dunlop.)

(6.) **Manganic Acid** ($H_2MnO_4 = 121$).—*The manganates.* The free acid is not known. *Potassic manganate* (mineral chameleon) (K_2MnO_4) and *sodic manganate* (Na_2MnO_4) are prepared by fusing together caustic potash or soda respectively, with manganese dioxide. The solutions when evaporated in vacuo over sulphuric acid yield green crystals. When these are dissolved in pure water, or in water containing a trace of acid (the manganates being less stable in an acid than in an alkaline solution), the salts are decomposed, the color of the liquid changing from green to red, due to the formation of potassic

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or sodic permanganate, a black precipitate of manganese dioxide being thrown down ($3K_2MnO_4 + 2H_2O = K_2Mn_2O_8 + MnO_2 + 2K_2H_2O_2$). The sodic manganate constitutes "*Condy's green disinfecting fluid*," the action of which depends on the ease with which the manganates yield their oxygen to organic matter. "Cassel green" is a baric manganate ($Ba''MnO_4$).

(7.) **Permanganic Acid** ($H_2Mn_2O_8$).—*The permanganates.*

Preparation.—(1.) A potassic permanganate is formed by the action of heat on an intimate mixture of manganese dioxide (4 parts), potassic chlorate (3·5 parts), and potassic hydrate (5 parts), whereby a potassic manganate is formed, which may be dissolved out with water. Carbonic anhydride is then passed through the green solution, until it becomes red ($3K_2MnO_4 + 2CO_2 = K_2Mn_2O_8 + 2K_2CO_3 + MnO_2$). The clear liquid decanted from the precipitate is then evaporated to a small bulk, and the potassic permanganate crystallised out (Béchamp). By treating the crystals with sulphuric acid, permanganic acid rises as a violet vapor, and may be condensed to a dark liquid.

(2.) A solution of the acid may also be prepared by decomposing baric permanganate with dilute sulphuric acid.

Potassic permanganate crystals appear red by transmitted, and dark green by reflected light. When heated they yield oxygen. All the permanganates (excepting the silver salt) are soluble in water, their solutions being of a red color. This color is discharged by sulphurous acid, by neutral solutions of the sulphides and pentathionates, by acid solutions of the sulphates, hyposulphites, arsenites, nitrites, etc., and by acid solutions of mercurous, ferrous, stannous, and antimonious salts, the permanganic acid being reduced to the colorless manganous oxide.

The permanganates are not so unstable as the manganates, nevertheless they readily yield their oxygen to organic matter, the permanganic acid first becoming manganic acid, and the manganese being ultimately reduced to the state of a hydrated manganic dioxide (Condy's red disinfecting liquid).

(8.) **Manganous Chloride**; *Protochloride of manganese* ($MnCl_2$).

Occurrence and Preparation.—It occurs mixed with ferric chloride in the residual liquor obtained during the preparation of chlorine. It may be separated by evaporating the clear filtrate to dryness and igniting, by which means the iron salt is either volatilized or converted by the remaining water into the insoluble sesquioxide. On treating the mass with water the manganous chloride may be dissolved out.

The salt is pink, deliquescent, soluble in water and alcohol, and fusible at a red heat.

(9.) **Manganic Chloride** (Mn_2Cl_6), a brown substance decomposed by heat ($Mn_2Cl_6 = 2MnCl_2 + Cl_2$). *Manganic tetrachloride* ($MnCl_4$), and *Manganic oxychloride* ($MnCl_2O_2$, Rose), (termed *Manganic perchloride*

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(Mn_2Cl_7) by Dumas), a yellowish condensible gas obtained by dissolving potassic permanganate in sulphuric acid, and adding fused sodic chloride to the solution, have also been described.

(11.) Manganous Sulphate ($MnSO_4,7H_2O$).

Preparation.—Manganic dioxide is first heated with sulphuric acid, the solution evaporated to dryness, and the residue ignited in order to decompose any ferric sulphate present. By acting on this residue with water, pure manganese sulphate is dissolved, and the insoluble ferric oxide left.

Properties.—A rose-colored soluble salt used by the dyer in producing blacks and browns.

(12.) Manganous Carbonate ($MnCO_3$) is found native as "manganese spar," and may be prepared as a hydrate ($2MnCO_3,H_2O$) by precipitating $MnCl_2$ with an alkaline carbonate.

Tests.—(*See* ANALYTICAL TABLES.)

ZINC (Zn″).

Atomic and Molecular weight, 65. *Specific gravity*, 6·8-7·2. *Atomicity dyad* (″) as ZnO; $ZnCl_2$.

History.—The metal was known (as "Spelter") in the thirteenth century. It was described by Paracelsus.

Natural History.—It has never been found native. It occurs as a *carbonate* ($ZnCO_3$) in calamine, as a *sulphide* in blende, as an *oxide* (ZnO) associated with iron and manganese oxides, in red zinc ore, and as a *silicate* in "electric calamine" or zinc glass (Williamite).

Preparation.—(A.) The ore is first brought into the state of oxide either (α) by *calcining* the carbonate or (β) by *roasting* the sulphide. Thus—

(α.) $ZnCO_3$ (calamine) $= ZnO + CO_2$.

(β.) $2ZnS$ (blende) $+ 3O_2 = 2ZnO + 2SO_2$.

(B.) The oxide is now heated with powdered coal, either, as in Silesia, in an earthen retort, or, as in England, in a crucible closed with a luted lid, into the bottom of which an exit pipe is fitted, through and down which the zinc distils (*distillation per descensum*).

$$ZnO + C = Zn + CO.$$

Impurities and purification.—Of the impurities of zinc the principal are *zinc oxide*, *lead*, *iron*, *tin*, *antimony*, *arsenic*, *copper*, and *cadmium*.

Zinc oxide is separated by melting the metal and skimming off the dross which collects on the surface, the ingots thus prepared being known commercially as "spelter." The presence of *lead* interferes with rolling the zinc. The greater specific gravity of lead (Pb=11·4; Zn=7·14) enables us to extract a portion of the lead from the mixed metal by simply melting the alloy, the *upper* part of the melted mass containing not more than 1·2 per cent. of lead.

Its separation from *cadmium* and *arsenicum* is commonly effected

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during its preparation. These metals being more volatile than zinc distil over first, and burn at the mouth of the tube with a brown flame (*brown blaze*). The distillation of the pure zinc is determined by the flame assuming a bluish-white color (*blue blaze*).

The pure metal may be prepared by igniting pure zincic carbonate, and distilling the oxide formed with sugar charcoal.

Properties.—(α.) *Physical.* A light, hard, bluish-white crystalline metal. It *melts* at 773° F. (412° C.), *boils* at 1,904° F. (1,040° C.), and *volatilizes* at a red heat. At ordinary temperatures it is *brittle;* between 212° and 302° F. (100° and 150° C.) it is both *ductile* and *malleable*, whilst at 410° F. (210° C.) it again becomes *brittle.*

(β.) *Chemical.* Zinc burns in air with a greenish-white flame, zincic oxide (ZnO) "*nil album*," or *philosopher's wool* being formed. The metal rapidly tarnishes in moist air, the zincic oxide formed protecting the metal underneath from further change. Cold water has no action upon it, but the metal decomposes steam ($Zn + H_2O = ZnO + H_2$). The haloid elements, in the presence of moisture, act freely upon it. All the acids attack it at ordinary temperatures. Solutions of the caustic alkalies act readily upon it, evolving hydrogen, zincic oxide, which is soluble in the alkaline solution, being formed ($Zn + 2KHO = ZnO,K_2O + H_2$).

Zinc is a powerful base; placed in many metallic solutions, it precipitates the metals, and in their stead is itself dissolved.

Hydrogen is commonly prepared by the action of dilute sulphuric acid on zinc. If *pure* zinc be used for this purpose, the evolution of hydrogen soon ceases, from the metal becoming covered with hydrogen globules. If a piece of copper be now introduced into the mixture, the copper (which is electro-negative towards the zinc) attracts the electro-positive hydrogen, and thus effects a continuous liberation of the gas.

Uses.—Zinc is employed in building operations, as a substitute for lead, its advantage being its comparative lightness. Although not malleable at common temperature, it is perfectly malleable at 212° F. (100° C.). *Galvanized iron* consists of iron coated with zinc, whereby we obtain the strength of the iron, which is much greater than that of zinc, together with the preservative action of the zinc, any ZnO formed, itself acting as a protective varnish. It is prepared by dipping *clean* iron into melted zinc covered with sal-ammoniac. By this means the surface of the melted zinc is kept free from oxidation, zinc oxide being soluble in NH_4Cl. If this were not done the zincic oxide adhering to the iron plate in the act of dipping would prevent its becoming uniformly coated. Zinc forms an alloy with iron and copper (brass), which alloy, with nickel, constitutes German silver.

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Compounds of Zinc.

SALTS.	Formula (Common).	Formula (Constitutional).	Molecular Weight of Anhydrous Compound.	Specific Gravity of Crystal.	= to Zn or ZnO per cent. of Anhydrous Salt.
1. Zincic oxide..	ZnO	**Zn**O	81	5·612	Zn = 80·24
2. „ hydrated oxide..	ZnH_2O_2	**Zn**Ho_2	99		Zn = 65·65
3. „ chloride	$ZnCl_2$	**Zn**Cl_2	136	2·753	Zn = 47·79
4. „ sulphide (blende)	ZnS	**Zn**S	97	4·1	Zn = 67·01
5. „ sulphate (white vitriol) ..	$ZnSO_4,7H_2O$	SOHo_2Zno″,6OH_2	161	Anhyd. 3·681 Crystal 1·931	Zn = 40·37
6. „ carbonate.. ..	$ZnCO_3$	**C**OZno″	125	4·4	ZnO = 64·8

(1.) **Zincic Oxide** (ZnO=81) is prepared by burning zinc in air. It is employed as a pigment (zinc-white) in the place of white lead, its advantage being that it is not blackened by sulphuretted hydrogen, and that its use does not affect the health of workpeople; whilst its disadvantage is, that it more easily peels off on account of its not combining chemically like oxide of lead with the oil. When heated the white oxide turns yellow, but it becomes white again as it cools. It is soluble in acids.

(2.) **The Hydrated Oxide** (ZnH_2O_2) is obtained by acting on solutions of zinc salts with potassic hydrate ($ZnSO_4+2KHO=ZnH_2O_2+K_2SO_4$), the precipitate being soluble in excess of the precipitant.

(3.) **Zincic Chloride** ($ZnCl_2$) is prepared either by dissolving zinc in hydrochloric acid, or by heating the metal in chlorine. By evaporating the solution, the chloride may be obtained as a white, deliquescent, fusible, corrosive solid. It is freely soluble in water and in alcohol. It absorbs ammonia gas freely. It distils at a red heat. It forms, with zincic oxide, a number of oxy-chlorides.

The solution (known as *Burnett's Disinfecting Fluid*) is a powerful antiseptic and deodorizer, from its capability of absorbing the offensive products of putrefaction. With the alkaline chlorides it forms double salts, the *zincic ammonic chloride* ($2H_4NCl,ZnCl_2$) being used as a flux in soldering, to remove the film of oxide from the surface of metals, such as zinc, iron or copper.

(4.) **Zincic Sulphide** (ZnS=97) occurs native as blende, either in masses, or in dark-colored crystals (rhombic dodecahedra). It may be obtained as *a white hydrated sulphide* by the action of hydric-ammonic sulphide on a solution of a zinc salt.

(5.) **Zincic Sulphate** (*white vitriol*, $ZnSO_4,7H_2O$).

Preparation.—By roasting zincic sulphide *at a low temperature.* [If roasted *at a high temperature* an oxide would be formed.] The mass is then dissolved in water and crystallised. It is also found as a residue in the common process of preparing hydrogen.

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Properties.—A white, crystalline (four-sided prisms), efflorescent salt, soluble in water (1 in 2·5 aq. at 60° F., and 1 in 1 at 212° F.). When heated it melts in its own water of crystallisation. At 212° F. it gives up $6H_2O$, and at 400° F. it becomes anhydrous. With potassic and ammonic sulphates it forms double salts, such as $ZnK_2(SO_4)_2,6H_2O$, these salts being isomorphous with the corresponding magnesium salts.

White vitriol is used in calico printing, and in medicine as an emetic.

(6.) Zincic Carbonate ($ZnCO_3=125$) is found native as calamine, so called from its tendency to form reed-like masses. The body termed "electric calamine" is a silicate.

When a soluble carbonate is added to a solution of a zinc salt, a *hydrated zincic oxycarbonate* is formed ($8ZnO,3CO_2,6H_2O$), which is soluble in ammonic carbonate, but not in the carbonates of soda or potash.

Tests.—(*See* ANALYTICAL TABLES.)

COBALT (Co″).

Atomic weight, 59. *Specific gravity*, 8·95. *Atomicity dyad, as in cobaltous compounds* ($Co''O$; $Co''SO_4$), *and tetrad (although apparently triad) in cobaltic compounds* $\left\{\begin{matrix} Co\equiv Cl_3 \\ | \\ Co\equiv Cl_3 \end{matrix}\right. = Co_2Cl_6$.

History.—Since the sixteenth century, roasted cobalt ores have been used for producing a blue glass. The metal was discovered by Brandt (1733).

Natural History.—It is never met with in a free state in nature, except in meteoric iron. It occurs as an *arsenide* as "tin white cobalt" ($CoAs_2$), and as an *arsenio-sulphide* in cobalt glance (CoAsS). Its ores commonly contain nickel, copper, iron, manganese, etc.

Preparation.—By heating cobaltic oxalate (CoC_2O_4).

Properties.—(α.) *Physical.* A white, hard metal, ductile and magnetic. It is very infusible, and possesses great tenacity.

(β.) *Chemical.*—It oxidises by exposure to air. The mineral acids act on it freely.

(1.) Cobaltous Oxide.—*Protoxide of Cobalt* ($Co''O$).

Preparation.—The hydrate (CoH_2O_2) is formed by precipitating cobaltous sulphate with sodic carbonate. If the precipitate be ignited, it leaves cobaltous oxide (CoO).

Properties.—A brown colored body, becoming the black cobaltic oxide (Co_3O_4) when first heated, but is reconverted into cobaltous oxide by a greater heat. It is soluble in acids, the solution being blue when concentrated, and pink when dilute. It is used for painting on porcelain. "*Thénard's blue*" is a compound of cobalt with alumina. "*Zaffre*" is a roasted mixture of cobalt ore and sand. "*Rinman's green*" is a compound of the oxides of cobalt and zinc. "*Smalt*" is powdered glass colored by oxide of cobalt (*see* page 335).

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Compounds of Cobalt.

SALTS.	General Formula.	Constitutional Formula.	Molecular Weight.	Special Gravity of Anhydrous Salts.	Co per cent.
1. Cobaltous oxide (protoxide)	CoO	$Co''O$	75		78·66
2. Hydrated cobaltous oxide..	CoH_2O_2	$CoHo_2$	93		63·44
3. Cobaltic oxide (sesquioxide)	Co_2O_3	$\left\{\begin{matrix}CoO\\O\\CoO\end{matrix}\right.$	166		71·08
4. Cobaltoso-cobaltic oxide ..	CoO,Co_2O_3	$\left\{\begin{matrix}CoO\\CoO\end{matrix}\right.Coo''$	241		73·44
5. Cobaltous chloride	$Co''Cl_2$	$CoCl_2$	130		45·38
6. Cobaltic chloride	Co_2Cl_6	$\left\{\begin{matrix}CoCl_3\\CoCl_3\end{matrix}\right.$	331		35·64
7. Sulphides (protosulphide)	CoS	CoS	91		64·83
8. Sulphides (sesquisulphide)	Co_2S_3				
9. Sulphides (disulphide ..	CoS_2	CoS_2	123		
10. Cobaltous sulphate	$Co''SO_4,7H_2O$	$SOHo_2Coo'',6OH_2$	155	3·531	$\left\{\begin{matrix}CoO=48·39\\Co=38·06\end{matrix}\right.$
11. Cobaltous nitrate	$Co2NO_3,6H_2O$	$\left\{\begin{matrix}NO_2\\NO_2\end{matrix}\right.Coo''6OH_2$	183	1·83	32·24
12. Cobaltous carbonates..	$5CoO,2CO_2,4H_2O$ $4CoO,2CO_2,5H_2O$ $3CoCO_3,2H_2O$				

(3.) Cobaltic Oxide, or *sesquioxide of cobalt* (Co_2O_3).

Preparation.—(1.) *As a hydrate* (Co_2O_3, $3H_2O$). By passing chlorine through water in which hydrated cobaltous oxide is suspended ($3CoH_2O_2 + Cl_2 = Co_2H_6O_6 + CoCl_2$).

(2.) *Anhydrous.*—By igniting the hydrate at a gentle heat.

Properties.—A black, insoluble substance. At a high temperature it becomes (CoO,Co_2O_3). It is a feeble base, the acid solutions gradually becoming salts of the protoxide.

(5.) Cobaltous Chloride ($CoCl_2$).

Preparation.—(1.) By passing chlorine over the metal.

(2.) By dissolving the oxide in hydrochloric acid.

Properties.—The anhydrous cobaltous chloride is *blue*, and the hydrate $CoCl_2,6H_2O$ is *red.* The "*blue sympathetic ink*" is a dilute solution of this salt, the change of color depending on different degrees of hydration. The addition of traces of zinc, iron or copper chlorides, varies the tints produced.

(6.) Cobaltic Chloride (Co_2Cl_6) is prepared by saturating $CoCl_2$ with chlorine.

(11.) Cobaltous Nitrate ($Co2NO_3,6H_2O$).

Preparation.—By dissolving the oxide in nitric acid.

Properties.—It is used as a blow-pipe reagent. When a *zinc* com-

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pound is moistened with it and heated it turns green, a *magnesium* compound turning pink, and an *aluminium* compound blue.

By treating cobaltous salts *protected from the air* with ammonia, crystallizable rose-coloured compounds (*ammonio-cobaltous salts*) are formed, as, *e. g.*, ($CoCl_2$,$6NH_3$,$3H_2O$). If this mixture be *exposed to the air* the solution absorbs oxygen, and brown compounds (*peroxidized ammonio-cobalt salts*) of a very complex nature result, consisting of ammonia and various oxides of cobalt.

Tests for Cobalt.—(*See* ANALYTICAL TABLES.)

NICKEL (Ni″).

Atomic weight, 59. *Specific gravity*, 8·7. *Atomicity dyad, as in nickelous compounds* ($NiCl_2$), *and tetrad* (*although apparently triad*) *in nickelic compounds, as* Ni_2O_3.

History.—Discovered by Cronstedt (1751).

Natural History.—It is found as an *arsenide*, as kupfernickel (NiAs) and arsenical nickel ($NiAs_2$); and also as an *arsenio-sulphide* as grey nickel ore or nickel glance ($NiAs_2$,NiS_2). It occurs in meteorites. It is always associated in nature with cobalt.

Preparation.—(1.) By roasting cobalt ore, an oxide of cobalt is formed. When this is fused with quartz and potassic silicate, it forms a blue glass (smalt), consisting of a mixture of the silicates of cobalt and potash. The fused metallic residue which collects at the bottom of the crucible, constitutes "*speiss*," a mixture of the sulphides and arsenides of nickel, iron, and copper. From this residue metallic nickel is obtained.

(2.) By igniting the oxalate.

Properties.—(α.) *Physical.* A hard, silvery-white metal, ductile and malleable, more fusible but of greater tenacity than iron. It is somewhat magnetic, a property it loses when heated to 626° F. (330° C.). Specific gravity, 8·8.

(β.) *Chemical.* It oxidizes when heated in air. Nitric acid dissolves it readily, and hydrochloric and dilute sulphuric acids slowly, hydrogen being evolved. It is acted on by chlorine and bromine.

Uses.—For rendering brass (an alloy of copper and zinc) white (*German silver*, *packfong*, *tutenag*).

(1, 2.) Nickelous Oxide.—*Protoxide of Nickel* (NiO).

Preparation.—(1.) (*Anhydrous*). By the ignition of the nitrate or carbonate.

(2.) *As a hydrate* (NiH_2O_2). By adding potassic hydrate to a solution of nickel salts.

Properties.—The hydrate, as well as its solution in acids, is green. It is soluble in ammonia and in ammonic chloride, but is insoluble in sodic and potassic hydrates.

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Compounds of Nickel.

SALTS.	Ordinary Formula.	Constitutional Formula.	Molecular Weight.	Specific Gravity.	Ni
1. Nickelous oxide (protoxide)	NiO	$\mathbf{Ni}O$	75	5·75	78·67
2. Hydrated nickelous oxide..	NiH_2O_2	$\mathbf{Ni}H_2O_2$	93		63·44
3. Sesquioxide of nickel ..	Ni_2O_3	$\left\{\begin{matrix}\mathbf{Ni}O\\O\\\mathbf{Ni}O\end{matrix}\right.$	166		71·08
4. Nickelous chloride	$NiCl_2$	$\mathbf{Ni}Cl_2$	130		45·38
5. Sulphides: subsulphide ..	Ni_2S	$'\mathbf{Ni}'_2S$	150		
6. Sulphides: protosulphide	NiS	$\mathbf{Ni}S$	91		64·83
7. Sulphides: disulphide ..	NiS_2	$\mathbf{Ni}^{iv}S_2$	123		
8. Nickelous sulphate	$NiSO_4,7H_2O$	$\mathbf{S}O_2Nio'',6H_2O$	155	2·037	38·06
9. Nickelous nitrate	$Ni2NO_36H_2O$	$\left\{\begin{matrix}\mathbf{NO}_2\\\mathbf{NO}_2\end{matrix}\right.Nio'',6H_2O$	183		32·24
10. Nickelous carbonate	$NiCO_3$	$\mathbf{C}ONio''$	119		49·57

(3.) The **Sesquioxide of Nickel** (Ni_2O_3) forms no salts with acids. It is decomposed by heat.

(6.) **Protosulphide of Nickel** (NiS) occurs native as "millerite" or "capillary pyrites," and is precipitated as a hydrate by the action of an alkaline sulphide on a salt of nickel.

(8.) **Nickelous Sulphate** ($NiSO_4,7H_2O$).

Preparation.—By dissolving the metal, or NiO, or $NiCO_3$, in sulphuric acid.

Properties.—A green crystalline salt (rhombic prisms), soluble in water (1 in 3 aq. at 60° F.), and insoluble in alcohol. It forms double salts with potassic and ammonic sulphates, which are isomorphous with the corresponding magnesium salts—

$$\left(NiSO_4\left\{\begin{matrix}K_2SO_4\\(NH_4)_2SO_4\end{matrix}\right.6H_2O\right)$$

Tests.—(*See* ANALYTICAL TABLES).

URANIUM (U).

Atomic weight, 240. *Atomicity, tetrad in Uranous compounds* (*as* UO_2; UCl_4), *and hexad in Uranic compounds* (*as* UO_3).

History.—Discovered by Klaproth.

Natural History.—It occurs as an *oxide* (pitchblende, UO,U_2O_3 with Cu, Pb, Fe, As, etc.), and as a *phosphate* (uranite and chalcolite).

Preparation.—By decomposing the chloride with metallic sodium or potassium.

Properties.—A greyish metal. It is not oxidized by air or by water at common temperatures, but burns in air when heated. It is soluble

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in sulphuric and in hydrochloric acids. It combines energetically with sulphur and chlorine.

Uses.—In enamel painting, and for coloring glass for optical and electrical purposes.

Compounds of Uranium.

SALTS.	Ordinary Formula.	Constitutional Formula.	Molecular Weight.	Specific Gravity.
1. Uranous oxide (protoxide)	UO_2	UO	256	
2. Uranic oxide (sesquioxide) or Uranyl oxide	UO_3	UO_3	288	
3. Other oxides: suboxide ..	U_2O_3	U_2O_3	528	
4. Other oxides: black oxide	U_2O_5, U_3O			
5. Other oxides: green oxide	U_3O_8			7·31
6. Uranous chloride (protochloride)	UCl_4			
7. Uranium oxychloride ..	UO_2Cl_2			
8. Uranic nitrate	$UO_2(NO_3)_2 6H_2O$			

Uranium forms two classes of compounds — *uranous* and *uranic* salts. Uranic oxide can act both as base and acid, forming in the latter case the compounds called *uranates*, which have the general composition $M'_2O, 2UO_3$.

Reactions of Uranium Compounds.

To the borax bead uranium imparts a yellow color in the oxidizing flame, and a green color in the reducing flame.

Solution.—(A.) *Uranous Compounds* (generally green).

(1.) *Alkalies*, a gelatinous brown ppt. (UO_2, H_2O), becoming, after a time yellow (UO_3).

(2.) *Ammonic Sulphide*, a black ppt. (uranous sulphide).

(B.) *Uranic Compounds* (yellow).

(1.) *Ammonia*, a yellow ppt. of ammonic uranate.

(2.) *Ammonic Sulphide*, a yellowish brown ppt.

To detect uranium in a mineral, dissolve the mineral in nitric acid, dilute with water, boil with an excess of sodic carbonate, filter, and precipitate the U_2O_3 with potassic hydrate.

INDIUM (In'').

Atomic weight, 113·4. *Specific gravity*, 7·4. *Fuses at* 349° F. (176° C.). *Atomicity* (''') *triad as in* $InCl_3$.

History.—Discovered by Reich and Richter in the Freiberg zinc blende (1863) by its peculiar spectrum, viz., the occurrence of two bright lines in the blue and indigo.

Natural History.—Indium is found in zinc blende and in other zinc ores, and also in the flue dust of zinc furnaces.

Extraction.—The blende is first acted upon with a quantity of dilute sulphuric acid, insufficient to effect its complete solution. The

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undissolved residue is then dissolved in nitric acid, and the lead and cadmium precipitated from the solution by sulphuretted hydrogen. After filtering and boiling (to expel the H_2S) baric carbonate is added to the filtrate, when the indic oxide (In_2O_3) is precipitated. This is dissolved in hydrochloric acid, and an excess of ammonia added. The white hydrated oxide ($In_2H_6O_6$) is thus thrown down, and may be reduced by heating in a stream of hydrogen.

Properties.—Indium is a white or lead-like metal, non-crystalline, soft, and ductile. It is less volatile than zinc or cadmium. It burns at a red heat with a violet flame, forming the yellow *indic oxide* (In_2O_3), but it does not oxidize readily below a red heat. It dissolves in acids.

Sulphuretted hydrogen precipitates in neutral solutions, or in solutions containing *acetic acid*, a yellow-coloured *sulphide* (In_2S_3). The alkalies and their carbonates give white precipitates.

Compounds of Indium.

SALTS.	Common Formula.	Constitutional Formula.	Molecular Weight, Anhydrous.	Specific Gravity.
Indic oxide (yellow oxide)	In_2O_3	$\left\{\begin{matrix}InO\\O\\InO\end{matrix}\right.$	274·8	
Indic chloride	In_2Cl_6	$\left\{\begin{matrix}InCl_3\\InCl_3\end{matrix}\right.$	439·8	
[Bromide and iodide analogous to chloride].				
Indic sulphide	In_2S_3	$\left\{\begin{matrix}InS\\S\\InS\end{matrix}\right.$	322·8	
Indic nitrate	$In_26NO_39H_2O$.		598·8	
Indic sulphate	$In_2(SO_4)_3,9H_2O$	$S_3O_6In_2O^{vi},9OH_2$	514·8	
Indic sulphite	$2In_2O_3,3SO_2,8H_2O$		741·6	

Reactions of Indium Compounds.

1. The metal is precipitated from the solution of a salt, by the action of metallic *zinc* or *cadmium*. The peculiar spectrum of indium has been referred to.

2. Boil with an excess of acid *sodic sulphite;* a precipitate is formed of sulphite of indium ($2In_2O_3,3SO_2,8H_2O$).

3. *Sulphuretted hydrogen;* a yellow precipitate (In_2S_3) in neutral solutions, or in solutions containing acetic acid.

4. *Alkaline hydrates and carbonates;* a white precipitate ($In_2H_6O_6$), soluble in excess of ammonic carbonate, or of the fixed alkaline hydrates.

5. *Heated on charcoal,* a ductile metallic bead of the metal may be obtained.

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CHAPTER XV.

GROUP IV.—THE METALS OF THE EARTHS.

IRON AND CHROMIUM.

ALUMINIUM ($Al''' = 27{\cdot}5$)—GLUCINUM ($G'' = 9{\cdot}5$)—YTTRIUM ($Y'' = 61{\cdot}7$)—ERBIUM ($E'' = 112{\cdot}6$) — CERIUM ($Ce''_{\bullet} = 92$) — LANTHANUM ($La'' = 92$) — DIDYMIUM ($Di'' = 96$)—THORINUM ($Th'' = 238$)—ZIRCONIUM ($Zr^{iv} = 89{\cdot}5$).
IRON and its Compounds—CHROMIUM and its Compounds.

ALUMINIUM ($Al = 27{\cdot}5$).

Specific gravity, 2·6. *Fuses at* 842° F. (450° C.). *Atomicity tetrad, and also pseudo-triad.*

History.—Discovered by Wöhler, 1828.

Natural History.—Next to silica, aluminium, as clay (*silicate of alumina*), is the most abundant of minerals. It has been found in certain cryptogamous plants, but practically it can scarcely be regarded as a constituent either of animals or vegetables.

Preparation.—(1.) By decomposing aluminic chloride (Al_2Cl_6) with sodium or potassium (Wöhler).

(2.) By the *electrolysis* of the double chloride of sodium and aluminium ($2NaCl, Al_2Cl_6$).

(3.) (Commercial.) By heating *bauxite* (a mineral containing 60 per cent. of Al_2O_3) with soda ash, whereby an aluminate of soda is produced ($3Na_2O, Al_2O_3$). On adding HCl to the solution of this compound, alumina is precipitated as a hydrate ($Al_2O_3, 3H_2O$). This precipitate is now mixed with common salt and carbon, and chlorine passed over the heated mixture, a sodic aluminic chloride distilling over ($2NaCl, Al_2Cl_6$). This compound is then heated with metallic sodium, when metallic aluminium and sodic chloride are formed.

Properties.—(α.) *Physical.* A white malleable ductile metal, crystallizing in regular octahedra. It conducts electricity with about one third the power of silver. It is a very light metal (2·5 Sp. Gr.), remarkably sonorous, and slightly magnetic. It melts when heated, but is not volatile.

(β.) *Chemical.* It does not oxidise readily either in steam or in hot or cold air, it being the lightest metal known difficult of oxidation. It burns in oxygen (forming Al_2O_3), and in the vapor of sulphur (forming Al_2S_3). Sulphuretted hydrogen is without action upon it; hence its value for ornaments. Nitric acid does not attack it when cold, and but very slightly even when boiling. Hydrochloric acid, cold or hot, dissolves it freely ($Al_2 + 6HCl = Al_2Cl_6 + 3H_2$). Alkalies act energetically upon it, liberating hydrogen. It combines with carbon and with

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silica. It forms alloys with silver, iron and copper (aluminium bronze), but neither alloys itself with lead, nor forms an amalgam with mercury.

Compounds of Aluminium.

SALTS.	Formula (Common).	Formula (Constitutional.)	Molecular Weight of Anhydrous Compound.	Specific Gravity (Crystal).	= Al_2O_3 or Al per cent.
1. Aluminic oxide (alumina)	Al_2O_3	$\left\{\begin{matrix}\mathbf{Al}O\\O\\\mathbf{Al}O\end{matrix}\right.$	103	3·95	Al_2O_3=100·00
2. Aluminic chloride.	Al_2Cl_6	$\left\{\begin{matrix}'\mathbf{Al}'''Cl_3\\'\mathbf{Al}'''Cl_3\end{matrix}\right.$	268		Al = 20·52
3. ,, bromide.	Al_2Br_6	$\left\{\begin{matrix}'\mathbf{Al}'''Br_3\\'\mathbf{Al}'''Br_3\end{matrix}\right.$	535		Al = 10·28
4. ,, iodide...	Al_2I_6	$\left\{\begin{matrix}'\mathbf{Al}'''I_3\\'\mathbf{Al}'''I_3\end{matrix}\right.$	817		Al = 6·73
5. ,, fluoride.					
6. ,, sulphide.	Al_2S_3	$\left\{\begin{matrix}\mathbf{Al}S\\S\\\mathbf{Al}S\end{matrix}\right.$	151		Al = 36·42
7. Trisodic aluminate	$Na_6Al_2O_6$	$\left\{\begin{matrix}\mathbf{Al}Nao_3\\\mathbf{Al}Nao_3\end{matrix}\right.$	289		Al = 19·03
8. Aluminic sulphate.	$Al_23SO_4,18H_2O$	$S_3O_6Al_2O^{vi},18OH_2$	343	1·671	Al_2O_3= 30·02
9. Potassic aluminic sulphate (alum)	$K_2Al_24SO_4,24H_2O$	$\left\{\begin{matrix}\mathbf{S}O_2Ko\\\mathbf{S}O_2Al_2O^{vi},24OH_2\\\mathbf{S}O_2Ko\end{matrix}\right.$	517·2	1·726	Al_2O_3= 19·91
10. Aluminic phosphates	$Al_2P_2O_8$	$\mathbf{P}_2O_2Al_2O^{vi}$	245		Al_2O_3= 42·04
11. ,, silicates..					

(1.) Aluminic Oxide.—*Alumina* (Al_2O_3). This is the only oxide of aluminium. It occurs native as "corundum" (the next hardest body to diamond), as "emery," as the "ruby" and "sapphire" (colored with a chromium salt), as the "spinelle" (MgO, Al_2O_3), and the "topaz" (a compound of alumina, silica, and aluminic fluoride). *Diaspore* ($Al_2O_3H_2O$) and *Gibbsite* ($Al_2O_3,3H_2O$) are native hydrates.

Preparation.—(1.) (As a hydrate, $Al_2O_3,3H_2O$) By adding ammonia to an alum solution.

(2.) (Anhydrous.) By the ignition of pure ammonia alum.

Properties.—The hydrate ($Al_2H_6O_6$) when first precipitated is a bulky transparent gelatinous precipitate, contracting as it dries to a gummy hygroscopic mass This mass when ignited loses its water, and absorbs a large quantity of heat, on account of which property it is used for the purpose of filling the spaces between the iron plates of fire-proof safes. *Before* being dried the hydrate is very soluble both in hydrochloric acid and in potassic hydrate solutions; but *after* drying it is almost insoluble in either the one or the other. It fuses by heat, forming a colorless transparent mass.

Alumina is capable of acting both as a base and as an acid. Thus,

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as a *base* it forms salts with acids, such as aluminic sulphate, all of which salts have an acid reaction, and are easily decomposed. As an *acid* it combines with basic oxides, forming a class of salts known as the aluminates. Thus the *spinelle ruby* is a magnesic aluminate (MgO,Al_2O_3), *gahnite* a zincic aluminate (ZnO,Al_2O_3). A potassic aluminate has also been obtained (K_2O,Al_2O_3).

Alumina combines with silica to form clay.

Aluminic hydrate combines with certain organic coloring matters, forming a class of pigments called "*lakes*." Thus alum is used as a *mordant* to fix coloring matters on calico.

(2.)—Aluminic Chloride.—(Al_2Cl_6). Specific gravity of vapor, 9·27.

Preparation.—(1.) By passing chlorine over a mixture of carbon and alumina heated to redness ($Al_2O_3+C_3+3Cl_2=Al_2Cl_6+3CO$).

(2.) By heating clay in a mixture of hydrochloric acid gas and the vapor of carbonic disulphide.

[NOTE.—Aluminic chloride cannot be prepared by dissolving Al_2O_3 in HCl and evaporating. A hydrate of aluminic chloride is formed in solution ($Al_2Cl_6,12H_2O$), but this on evaporation evolves HCl, leaving Al_2O_3.]

Properties.—A yellow, crystalline, deliquescent body, emitting fumes of HCl when exposed to the air. It is soluble in alcohol, and dissolves with a hissing noise in water. It melts and sublimes when heated. It combines with ammonia, with phosphoretted hydrogen, and with sulphuretted hydrogen.

"*Chloralum*" is an impure aluminic chloride.

(5.)—Aluminic Fluoride.—(Al_2F_6) is found native as *cryolite* ($6NaF,Al_2F_6$), and as *topaz* $2(Al_2O_3,SiO_2),Al_2O_3SiF_4$).

(8.)—Aluminic Sulphate.—($Al_23SO_4,18H_2O$) may be obtained by dissolving alumina in sulphuric acid. It is prepared commercially by heating clay with sulphuric acid. The clear solution, after being first freed from iron by potassic ferrocyanide, and afterwards evaporated to a syrup, is known to the dyers as "*concentrated alum*," or when reduced to the solid state as "*cake alum*." The crystals are exceedingly soluble.

(9.)—Potassic Aluminic Sulphate.—*Alum* ($K_2Al_24SO_4,24H_2O$).

Natural History.—Found native in volcanic districts, produced by the action of volcanic sulphuric acid on the aluminium compounds of the rocks.

Preparation.—(1.) (α.) "Alum shale," a compound of aluminic silicate, iron disulphide, and bituminous matters, is first roasted, whereby one-half of the sulphur of the FeS_2 becomes oxidized. Thus,

$$2FeS_2 + 3O_2 = 2FeS + 2SO_3.$$

Ferric disulphide + Oxygen = Ferrous sulphide + Sulphuric anhydride.

(β.) When water is added to the residue, the SO_3 becomes H_2SO_4, which immediately decomposes the aluminic silicate forming aluminic sulphate.

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(γ.) By exposure to air the ferrous sulphide becomes ferrous sulphate.

(δ.) When the mass is lixiviated, a solution results (called crude alum liquor), containing alumina and ferrous sulphate, and also probably some magnesic sulphate.

(ε.) Part of the ferrous sulphate is now removed by crystallization.

(ζ.) Potassic chloride (in the form of soap boilers' waste, or the refuse of glass houses or of saltpetre refineries) is now added to the solution, whereby any ferrous sulphate is decomposed, and a soluble ferrous chloride, together with potassic sulphate, formed.

$$2KCl + FeSO_4 = FeCl_2 + K_2SO_4.$$

Potassic chloride + Ferrous sulphate = Ferrous chloride + Potassic sulphate.

(η.) The potassic sulphate as soon as formed, combines with the aluminic sulphate to form "*potash alum*," which being sparingly soluble in cold water is deposited from the solution as "alum meal" or "alum flour." This is afterwards washed with cold water to remove adherent iron. It is subsequently crystallized.

Very frequently ammonic sulphate (from gas liquor) is used instead of potassic chloride, in which case *ammonia alum* is formed, $(NH_4)_2Al_24SO_4,24H_2O$.

If *sodic sulphate* be employed, *soda alum* is formed, $Na_2Al_24SO_424H_2O$. Thus we may obtain by the employment of different reagents a series of alums, some of which we have tabulated as follows :—

Potash alum	$K_2Al_24SO_4,24H_2O$.
Soda alum	$Na_2Al_24SO_4,24H_2O$.
Ammonia alum	$(H_4N)_2Al_24SO_4,24H_2O$.
Iron alum	$K_2Fe_24SO_4,24H_2O$.
Chrome alum	$K_2Cr_24SO_4,24H_2O$.
Manganese alum...	$K_2Mn_24SO,24H_2O$.

Further, a silver-alum, a cæsium-alum, and a thallium-alum may be obtained.

(2.) By burning "*alum stone*." The alum thus prepared is known as "*Roman alum*."

Properties.—Alum is a white, crystalline (octahedra) astringent-tasted body, soluble in water (1 in 18 aq., at 60° F., and 1 in 1 at 212° F.). Its solution has an acid reaction, and dissolves iron and zinc with the evolution of hydrogen. When alum is first heated, it melts in its own water of crystallization. At 392° F. (200° C.) the water evaporates, and the residue swells up to a white infusible and insoluble mass called *burnt alum* ($K_2Al_24SO_4$). By ignition, some of the acid of this alum may be expelled. It is but little affected by exposure to air. *Homberg's pyrophorus* is a mixture of alum and sugar, carbonized out of contact with air.

Alum is largely used in dyeing, in the preparation of skins, and in medicine.

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We have in the *alums* a marked illustration of isomorphism, that is of bodies of different chemical composition, crystallizing in the same form. *Potash alum* forms white octahedra; *chrome alum*, dark red octahedra; *iron alum*, violet octahedra, etc.

(10.) Aluminic Phosphates are found as natural minerals, as, *e.g.*, turquoise, which is a hydrated phosphate, colored with copper and iron ($2Al_2O_3,P_2O_5,5H_2O$); wavellite, $3(4Al_2O_3,3P_2O_5,18H_2O),Al_2F_6$; lazulite (a double phosphate, colored with phosphate of iron), etc.

(11.) Aluminic Silicates.—These are both numerous and complicated. Their complication arises from the frequent replacement of Al_2O_3 by the isomorphous body, Fe_2O_3, other metals present being similarly exchanged for their isomorphous representatives.

A few of these silicates are stated in the following table :—

	Garnet (Ca,Al,Mg,Fe and Mn)	$3(CaMgFeMn)O(AlFe)_2O_3 3SiO_2$.
	Chlorite (Al,Mg, etc.)	$4(MgFe)O,(AlFe)_2O_3,2SiO_2,3H_2O$.
	Basalt (Ca,Mg)	$4(CaMgFe)O 5SiO$.
	Cyanite, Diothene	Al_2O_3,SiO_2.
Zeolites	Analcime (Na,Al)	$Na_2O,Al_2O_3,4SiO_2,2H_2O$.
Zeolites	Stilbite (Ca,Al)	$CaO,Al_2O_3,6SiO_2,6H_2O$.
Zeolites	Prehnite (Ca,Al)	$2CaO,Al_2O_3,3SiO_2H_2O$.
Felspar	Potash * Felspar (orthocluse)	K_2
Felspar	Sodium ,, (albite)	Na_2
Felspar	Lithium ,, (petalite)	L_2
Felspar	Calcium ,, (Labradorite)	Ca — $O,Al_2O_3,6SiO_2$.
Mica	Uniaxial (Mg and Al)	$[4(MgKFe)O,(AlFe)_2O_3,4SiO_2]$.
Mica	Biaxial: K in excess	
Mica	Biaxial: Li in excess (Lepidolite)	$\left[\left(\begin{matrix}K\\Li\end{matrix}\right)Fe\right)O,3(AlFe)_2O_3,6SiO_2\right]$

Slate is an aluminic silicate of varied composition. *Roofing slate* is an argillaceous rock; *mica slate* contains mica, and *hornblende* slate, hornblende. *Granite* and *gneiss* consist of quartz, felspar and mica; *porphyry* is a felspar, so also is *basalt*, the latter containing crystals of augite. *Dolerite, greenstone, diorite, trachyte, fuller's earth, pumice stone*, which, in a melted state, is called *volcanic glass*, or *obsidian*, are also aluminic silicates.

Lapis lazuli or *native ultramarine* consists of a silicate of alumina mixed with lime, soda, sulphuric acid, sulphur and iron. The cause of its blue color is not well understood. *Artificial ultramarine* is prepared by heating together a mixture of 100 parts of kaolin, 100 of sodic carbonate, 160 of sulphur, and 12 of carbon. A green body results, which, on being further roasted with fresh sulphur, forms a brilliant blue mass. Ultramarine is bleached by acids and by chlorine. It is often used as the coloring matter for blue paper, which consequently becomes white when dipped in an acid.

Clay.

Formation.—The disintegration of granite rocks which consist of quartz, feldspar and mica, is both mechanical and chemical. By the action of air and by the expansion of the water in the rock during

* *Pericline* is an admixture of potash and soda felspar.

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congelation, it is gradually broken down. From this debris, water containing carbonic acid dissolves the potash, leaving quartz and silicate of alumina. These bodies are afterwards mechanically separated by water owing to their different gravities, the silicate of alumina being comparatively light. This, when deposited, constitutes *clay* ($Al_2O_3,2SiO_2,2H_2O$).

Composition of clay.—This varies considerably, as the following diagram shows :—

	Washed Kaolin.			Stourbridge Fire Clay.	Pipe Clay.	Sandy Clay.	Blue Clay.	Brick Clay.
	Chinese.	S. Yrieix.	Cornish.					
Silica	50·5	48·37	46·32	64·10	53·66	66·68	46·38	49·44
Alumina.. ..	33·7	34·95	39·74	23·15	32·00	26·08·	38·04	34·26
Oxide of iron..	1·8	1·26	0·27	1·85	1·35	1·26	1·04	7·74
Lime	—	—	0·36	—	0·40	0·84	1·20	1·48
Magnesia ..	0·8	trace	0·44	0·95	trace	trace	trace	5·14
Potash or soda.	1·9	2·40	} 12·67	10·00	12 08	5·14	13·57	1·94
Water	11·2	12·62						
	99·9	99·60	99·80	100·05	99·49	100·00	100·23	100·00

From MILLER.

Loam is a clay containing ferric oxide, whilst *marl* is a clay containing carbonate of lime. *Umber, red-bole, ochre* and *sienna*, are also clays containing various iron and manganese oxides.

Properties.—A tenacious mass, insoluble in, but capable of diffusion through water, very plastic, but shrinking when dried. It has a characteristic odor, and possesses great absorbent powers. It consequently retains the ammonia from manure when placed on the earth, storing it up for the vital functions of the plant. It also purifies water impregnated with organic impurities when passed through it. (Way.)

Clay is decomposed by sulphuric acid (*see* Preparation of Alum), but is very slowly acted upon either by hydrochloric or by nitric acids. After clay has been ignited, no acid, except hydrofluoric acid, has the least action upon it. It is slightly soluble in a solution of potassic hydrate, but becomes very soluble in water after its fusion with potassic hydrate.

Porcelain and Pottery.

Clay is employed in the manufacture of all kinds of pottery. Although plastic, it shrinks considerably when baked. To prevent this shrinking, sand, chalk, or bone-ash is mixed with the clay, but inasmuch as this has a tendency to disintegrate it, it is necessary afterwards to glaze it with some substance capable of vitrification, in order to cement the whole together and form it into a compact mass. This is the whole principle of the manufacture of pottery.

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(1.) *Bricks, coarse tiles, pipes,* etc, are made from common clay, of which there are three kinds, (α.) *marly or chalky clay* *, used for pale bricks; (β.) *potter's clay*, used for bricks and tiles; (γ.) *fire clay*, which is nearly free from lime.

Process.—The clay is dug up in the autumn, and exposed to the air (weathered). The stones present in the clay are either crushed in a mill or are removed by puddling or other means. This done, the clay is mixed with sand and well kneaded. The mass is then ready to be fashioned into shape by hand or machinery, the articles so formed being first dried in the air, afterwards fired in kilns, and finally glazed with a mixture of clay and litharge, or iron scarf, etc.

The red color of bricks and tiles is due to the carbonate of iron present in common clay becoming converted into peroxide (Fe_2O_3) by the action of atmospheric oxygen.

(2.) *Common earthenware.*—One of three kinds of clay is employed in its manufacture, *viz.*, (α) *Dorsetshire clay*, (β) *Devonshire clay* (blue clay), or (γ) *pipe clay.*

The clay is first of all cleansed by machinery, and reduced to a state of pap. It is then run through fine sieves. To prevent after-contraction and unequal drying, it is mixed with a pap of ground flints, the mixture being called "*slip*" (1 part of flints to 5 parts of clay). This flint-pap is prepared by subjecting flints from the chalk to an intense heat, suddenly quenching them with water, and finally grinding them into a pap. The mixed mass of sand and clay is now cut into square blocks, and kept for some months in a damp place. In this way any organic matter present becomes oxidised, thus reducing the sulphates to sulphides. When required, the "slip" is kneaded by beating it on a board, so as to effect its perfect incorporation, and the removal of all air bubbles. This kneading process in England is effected both by machinery and by hand labor. In France it is done with mallets; in Egypt by the treading of men; and in China by the treading of cattle. The article, after being roughly fashioned is partially dried, at a temperature varying from 80° to 90° F., and then further finished,—handles attached, etc. It is afterwards baked in kilns, placed in cases called "saggars," when it becomes converted into a porous earthenware called "biscuit." The freshly-struck pattern, printed on wet soaped paper with a mixture of some metallic oxide and boiled oil, is now placed on the "biscuit," and well rubbed with a flannel rubber, so that the "biscuit" may completely remove the impression from the paper. As soon as the design is absorbed by the "biscuit," the paper is removed by wetting with a sponge. The "biscuit" is now dipped into a weak alkaline lye, in order to saponify the oil, and is afterwards glazed with some fusible material, such as a mixture of white lead, Cornish stone, ground flints, ground

* A marl is a clay containing a considerable quantity of calcic carbonate. If the alumina be in excess it is an *aluminous marl*, if the chalk, a *calcareous marl*.

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glass, chalk felspar, silicate of alumina and potash, and borax. It is finally baked or "fired" in the kiln, whereby the glaze is fused.

The colors on the earthenware are produced by various metallic oxides (*see* page 307), which form a colored glass with the glaze, whilst the metallic lustres are produced by gold, platinum, copper, brass, etc.

(3.) *Porcelain* is a finer variety of pottery It is of two kinds; (α.) The *hard* porcelain, such as is made at Sevres, Dresden, etc., is manufactured from *kaolin*, a very pure white clay, obtained from China, Cornwall, S. Yrieix near Limoges, etc., and from *china stone*, which consists of the silicates of alumina, potash and lime. The glaze used is a mixture of felspar and quartz, suspended in water in which the article is dipped. (β.) The *soft* variety of porcelain as made in England contains bone earth.

The details of its manufacture are in all respects similar to that already described.

Wedgwood is a fine description of stoneware.

Salt Glazing, which is largely used in the preparation of stoneware, etc., is effected by throwing common salt into the furnace containing the heated articles, previously dipped into a mixture of sand and water. The salt volatilizes, and is decomposed by the sand on the hot surface of the ware. A fusible impervious silicate is thus formed as a glaze, hydrochloric acid escaping as vapor with the excess of salt ($H_2O + 2NaCl + SiO_2 = 2HCl + Na_2O,SiO_2$).

Tests.—(*See* ANALYTICAL TABLES.)

GLUCINUM. Beryllium (G″=9·5. *Specific gravity* 2·1).

History and Preparations.—Glucinum is found combined with silica and alumina in the *emerald* ($3GO,Al_2O_3,6SiO_2$), also in the *beryl*, colored with chromium, and in the *chryso-beryl* (GO,Al_2O_3). The metal may be prepared by a similar process to that described in preparing aluminium.

Properties.—A white, fusible, malleable metal. It does not burn in air, oxygen, or in sulphur, but it combines readily with chlorine, iodine, and silicon. It does not decompose steam. It is soluble in dilute sulphuric and in hydrochloric acids, but is insoluble in nitric acid. It is dissolved with the evolution of hydrogen by a solution of KHO. It forms one oxide (GO). Its salts are colorless, sweet (γλυκὺς), and acid to litmus.

YTTRIUM (Y=61·7); ERBIUM (Er=112·6).

These are rare metals found in gadolinite. They form the oxides yttria (YO) and erbia (ErO=128·6).

CERIUM (Ce=92).

Cerium is found in cerite (a silicate of cerium) and in brown apatite. Its oxalate is useful for the relief of the sickness of pregnancy.

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LANTHANUM (La=90·2).

Lanthanum is also found in cerite. It forms one oxide (LaO), which is buff-colored.

DIDYMIUM (Di=96).

Didymium is also found in cerite. It forms one oxide (DiO).

THORINUM (Th=231·5. *Specific gravity* 7·8).

Thorinum was discovered by Berzelius (1829) in the mineral thorite. It is prepared by reducing the chloride with potassium. It is a grey powder, incapable of decomposing water, but burning in air, forming thorina (ThO. Specific gravity=9·4). It is not acted on by the caustic alkalies, but is soluble in most acids.

ZIRCONIUM (Zr=89·6. *Specific gravity* 4·15).

Zirconium is found in nature as an oxide (Zirconia, ZrO_2), and also combined with silicic acid in zircon and in hyacinth (ZrO_2,SiO_2).

Properties.—Like silicium, to which it is closely allied, it exists in three states—(1.) an *amorphous* state, which burns when heated in the air below redness, forming zirconia (ZrO_2); (2.) a *crystalline* state, which requires the oxy-hydrogen heat to fire it; and (3.) the *graphoidal* state.

Zirconium has never been fused. It decomposes water slowly at the boiling point. It is acted on by hydrofluoric acid with the evolution of hydrogen, and also by aqua regia. It is insoluble in dilute sulphuric or hydrochloric acids.

It forms one *oxide*, zirconia (ZrO_2=121·5. Specific gravity 4·5) which, unlike alumina, is insoluble in the caustic alkalies. It is soluble in potassic carbonate. It acts both as a base and as an acid, in the latter case forming the compounds called *zirconates* (as Na_2ZrO_3).

Zirconic chloride ($ZrCl_4$=231·5) and *zirconic fluoride* (ZrF_4) have been prepared.

IRON (Fe″=56).

Atomic weight, 56. *Specific gravity*, 7·8. *Atomicity dyad* (″), *as in Ferrous salts* ($Fe''Cl_2$; $Fe''SO_4$), *and tetrad* (iv) *in Ferric salts, although apparently a triad, thus,* $\begin{matrix} FeCl_3 \\ | \\ FeCl_3 \end{matrix} = Fe_2Cl_6$.

Natural History.—Found *native* in meteorites, together with Ni, Co, Mn, Cu, etc., and is also found accompanying platinum ores. In *combination* it occurs in great abundance in numerous ores, as follows:—

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Iron Ores.

Common Names—Locality.	Formula and Composition.	Specific Gravity of Ore.
Magnetic iron ore; Loadstone; Iron-sand (India)	Fe_3O_4	5·09
Red hæmatite (Cornwall). (*Red ochre* contains clay)	Fe_2O_3	5·0
Specular iron; Fer oligiste; Iron glance (Elba, Russia, Sweden)	Fe_2O_3	5·2
Brown hæmatite; Pea iron ore; yellow ochre (France)	$2Fe_2O_3,3H_2O$	3·9
Spathic iron (Saxony)	$FeCO_3$	3·8
Clay ironstone (Great Britain, America) ..	$FeCO_3$, with clay.	2·7 to 3·47
Black-band (Scotland)	$FeCO_3$, with bituminous matters (20 to 30 per cent.)	
Iron pyrites	FeS_2	
Siliceous ironstone (Northampton) ..	Fe_2O_3 and $FeCO_3$	
Bog iron ore..	$2FeO_3,3H_2O$, and a ferric phosphate.	

The following table from Bloxam, compiled from analyses given in Percy ("On Iron and Steel,") shows the composition of most of the English iron ores:—

In 100 parts.	Iron.		Oxide of Manganese.		Phosphoric acid.		Bisulphide of iron.		No. of samples analysed.
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	
Clay iron stone from coal measures ..	43·30	20·95	3·30	0·46	1·42	0·07	1·21	..	77
Clay iron stone from the Lias	49·17	17·34	1·30	..	5·05	..	1·60	..	12
Brown hæmatite ..	63·04	11·98	1·60	trace	3·17	..	0·30	..	23
Red hæmatite ..	69·10	47·47	1·13	trace	trace	trace	0·06	..	5
Spathic ore	49·78	13·98	12·64	1·93	0·22	..	0·11	..	6
Magnetic ore.. ..	57·01		0·14		0·10		0·07		1

Preparation.—In England iron is usually manufactured from clay iron-stone.

(*α.*) The broken ore is first *roasted* or *calcined*, either in kilns, like lime-kilns, or in heaps exposed to the open air, whereby water, carbonic anhydride, and some sulphur is expelled, and an impure ferric oxide obtained.

(*β.*) This calcined ore is now *smelted* in the *blast furnace*.

The iron blast furnace is a brick building, some 50 or 60 feet high, closed at the bottom, and open at the top for the reception of the charge. Air is forced into the bottom of the furnace through three air-pipes or *tuyères*, whereby a high temperature is maintained. At

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the bottom certain tap-holes are placed, through which the melted iron may be let out, as well as other holes to allow the overflow of the slag.

The furnace is charged with layers of calcined iron ore, small-coal and limestone, fresh layers being introduced as required.

Principle of the blast furnace.—The *coal* burns at the expense of the oxygen of the air supplied through the air-pipes. The CO_2 thus formed passes over the hot fuel, and taking up more carbon becomes CO. This carbonic oxide coming into contact with the red-hot oxide of iron, becomes oxidized at the expense of its oxygen, leaving the iron in a metallic state. The heated iron, as it sinks in the furnace, combines with a little carbon, and so forms fusible "*cast iron*," which, in the hottest part of the furnace, reduces the silica and the phosphates, and combines with the silicon and phosphorus set free.

The *limestone* ($CaCO_3$), when heated, parts with its CO_2, leaving lime (CaO). This combines with the infusible clay (silicate of alumina) and with other impurities in the melted iron, to form a readily fusible double silicate of lime and alumina, which, owing to its less gravity, floats on the surface of the melted iron, and solidifies, when cold, to "*a slag*." [This limestone is called "*a flux*" because it makes the clay flow (*fluo*).]

Thus the melted metal, with the fused slag swimming on its surface, collects on the hearth of the furnace. The *slag* is allowed to run out of openings in the *upper* part of the hearth, whilst the *metal* is drawn off from below into sand-channels, each channel of iron being called "*a pig*" ("pig-iron"). The iron thus obtained is known as "cast-iron."

The gas issuing from the chimney of the furnace is highly inflammable and poisonous. The following represents its percentage composition:—

Nitrogen	55·35 vols.		
Carbonic oxide ...	25·97 ,,		
Hydrogen	6·73 ,,		
Carbonic acid ...	7·77 ,,		
Marsh gas	3·75 ,,		
Olefiant gas	0·43 ,,	=	100·00 vols.

The air, previous to its being supplied to the furnace through the "tuyères," is usually heated to 600° F. (315·5° C.) by this furnace gas. This constitutes what is called the "hot blast." In this way a great loss of heat is prevented. It is stated, however, that "*hot blast iron*" is of inferior quality to "*cold blast iron*," as the iron both receives and retains a larger quantity of impurities.

Cast iron (pig iron) contains about 2 to 5 per cent. of carbon, but it is not a pure carbide (Fe_4C).

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Composition of Cast Iron (Percy).

	Maximum.	Minimum.
Carbon ...	4·81 ...	1·04 per cent.
Silicon ...	4·77 ...	0·08 ,,
Sulphur ...	1·06 ...	0·00 ,,
Phosphorus ...	1·87 ...	trace ,,
Manganese ...	6·08 ...	trace ,,
Iron	81·41 ...	98·88 ,,

There are several varieties of cast iron known in commerce. In *white iron* (the color of which is due to manganese) the carbon exists in chemical combination with the metal (Sp. Gr. 7·53). In *grey iron* a portion of the carbon is present in an uncombined state (Sp. Gr. 6·92). *Mottled iron* is an intermediate variety between white and grey iron. *Cast iron* fuses at about 3000° F. (1648·8° C.). It is hard, non-elastic, and brittle. It cannot be welded.

Wrought iron.—Cast iron is changed into wrought iron by the processes of "*refining*" and "*puddling.*"

Refining is for the purpose of effecting the removal from the iron of the carbon, silicon, sulphur, and phosphorus. The melted metal is subjected to the action of a current of air, whereby the silicon and a part of the carbon become oxidised. The silica unites with the oxide of iron produced simultaneously, to form a fusible slag.

Puddling.—The puddling furnace is a reverberatory furnace; its use is rendered necessary by the circumstance that the metal becomes less fusible as it approaches purity. The fused metal is well *stirred* or "*puddled,*" so that the oxidation of the impurities may be effected by their actual contact with oxide of iron. The metal is then well hammered, in order to squeeze out the liquid slag. This hammered mass constitutes *wrought iron.*

The Bessemer process was invented to save the great manual labor involved in the ordinary puddling operation. It consists in burning out the carbon and silicon with an air blast, and then supplying carbon by the addition of sufficient cast iron (spiegel-eisen) to convert the whole into steel.

Wrought iron is soft, elastic, malleable and ductile. It is very difficult to melt, but is capable of being welded. It is magnetic.

Steel is prepared by embedding bars of wrought iron in charcoal and heating them for several days at 2000° F. (1093·3° C.) (Cementation). From the *fibrous* structure peculiar to wrought iron, the metal gradually assumes the *granular* structure peculiar to steel. This change is due to the iron throughout the mass becoming combined with about 1 per cent. of carbon. The transference of this carbon is believed to be effected by the formation in the first instance of carbonic oxide, half

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of the carbon of which is taken up by the iron ($2CO—C=CO_2$), the CO_2 formed becoming again converted into CO by taking up more carbon. Graham has shown that iron has the power of absorbing or "occluding" six or eight times its volume of carbonic oxide.

The unevenness of the *blistered steel* thus formed is remedied by hammering, whereby *shear steel* is produced. When this is heated to redness, and suddenly cooled by dipping into water or into oil, the steel is rendered very hard, brittle and elastic, its volume being slightly increased. By a process of tempering, that is, by again heating and cooling the steel, it is prepared for the various purposes for which it is required, the temper depending on the temperature of the metal when dipped, and on the rapidity of cooling. Heated to 430° F. (221° C.), and cooled slowly (called *tempering to the yellow*), the steel becomes very hard, and is used for knives, etc.; but if heated to 550° F. (287·8° C.), and then cooled (called *tempering to the blue*), it becomes highly elastic, and is used for watch springs, etc.

Case hardening, or the superficial conversion of soft iron articles into steel, is effected by heating them in contact with bone-dust, or other substance containing carbon, and then chilling them by dipping into water.

Steel, unlike iron, retains magnetism. Hence it is used in the manufacture of permanent magnets. A steel blade may be known from an iron blade by placing upon it a drop of dilute nitric acid. A dark stain will be produced on the face of the steel blade, from the separation of the carbon, whilst a green stain will result in the case of the iron blade.

Impurities.—These are *carbon* (0·2 to 0·5 per cent.) (the presence of which increases the hardness of the iron), *silicon*, *sulphur*, *phosphorus* and *arsenic*. The presence of the last four bodies is very objectionable.

Properties.—(*a.*) *Physical*. *Bar* iron is a hard, grey, lustrous metal; *pure* iron is soft and silvery. It has no smell unless it be rubbed. Its texture is fibrous. Its specific gravity is about 7·7. When heated it first becomes pasty, and in this condition may be welded.* At a greater temperature it may be fused. At a red heat it is both ductile and malleable. It expands slightly at the moment of cooling. Compared with other metals its tenacity is enormous, but its conductivity for heat and electricity is comparatively small. It is, in common with nickel and cobalt, but in a far higher degree than these metals, remarkably magnetic. A red heat, however, destroys its magnetism, although it recovers it again on cooling. Its magnetism, however, is not permanent, unless the iron be combined with *carbon*, as in steel, or with *oxygen*, as in Fe_3O_4, or with *sulphur*, as in Fe_3S_4, or Fe_7S_8, but combined with oxygen or sulphur in proportions other than these, the metal is not magnetic at all.

* In "welding," the two pieces of pasty metal are first covered with sand. This acts as a flux to the oxide, thus enabling two absolutely clean surfaces to be brought into contact. The slag of silica and oxide of iron formed is forced out by the hammering.

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(β.) *Chemical. Action of Air and Oxygen.—Dry* air has very little action on polished iron, but the metal rapidly rusts in *moist* air, forming $2Fe_2O_3,3H_2O$. The presence of carbonic anhydride expedites the rusting process by the formation of a carbonate of iron ($Fe+H_2O+CO_2=FeCO_3+H_2$), which is soluble in water containing CO_2, but is precipitated from its solution by the absorption of oxygen ($4FeCO_3+O_2=2Fe_2O_3+4CO_2$). Once started, the rusting process proceeds rapidly, owing to the hygroscopicity of the iron oxide. Rust always contains ammonia, formed by the direct union of the nascent hydrogen with atmospheric nitrogen. The contact of a nail with a wet cloth causes a diffused iron-mould stain, due to the formation of the carbonate of iron. Similarly the black streaks produced after a short time when iron nails have been driven into an oak fence are due to the action of the tannic acid of the oak on the solution of the carbonate of iron formed in the manner already indicated. When heated to a high temperature, iron burns in oxygen brilliantly, throwing out numerous scintillations. In a state of minute subdivision it fires on mere exposure to air.

Action of Water.—Iron is not acted on by water, when the water is free from air, but it is rapidly attacked by common water containing dissolved air, more especially if the water be exposed to air at the time of its contact with the iron. (*For the action, see above.*) The presence of a free alkali, or of an alkaline earth, or of an alkaline carbonate, interferes with this action. At a red heat iron decomposes water ($4H_2O+3Fe=Fe_3O_4+4H_2$).

Chlorine, bromine, and iodine, in the presence of water, combine rapidly with iron at ordinary temperatures.

Action of Acids.—Hot or cold concentrated sulphuric acid has a slight action on iron, SO_2 being liberated, whilst the dilute acid acts rapidly, evolving hydrogen. Ordinary nitric acid acts energetically upon the metal, N_2O_2 being evolved. If, however, the iron be first dipped in nitric acid of specific gravity 1·45, which is without action upon it, and then, without being wiped, placed in *dilute* nitric acid, the latter will be found to have no action on the metal. A similar change in the iron may also be effected by touching it, when immersed in a nitric acid of specific gravity 1·35, with a piece of gold or platinum, when the previous energetic action of the acid instantly ceases (*passive iron*). Hydrochloric acid acts freely on it, hydrogen being set free. Carbonic acid, dissolved in water freed from air, also rapidly attacks it, with the evolution of hydrogen. Thus, in most chalybeate waters the iron exists as a ferrous carbonate dissolved in water containing CO_2, a rusty deposit of oxide being formed when the water is freely exposed to the action of the air.

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Compounds of Iron.

		Common Formula.	Constitutional Formula.	Molecular Weight of Anhydrous Salt.	Specific Gravity of Crystals.	FeO in 100 parts.
1.	Oxides. Ferrous oxide (protoxide of iron)	FeO	**Fe**O	72		100
2.	Oxides. Ferric oxide (per- or red oxide)	Fe'''_2O_3	**Fe**O O **Fe**O	160		Fe=70·0
3.	Oxides. Magnetic or black oxide of iron	Fe_3O_4 or (FeO,Fe_2O_3)	**Fe**O **Fe**Oeo″	232	5·09	Fe=72·41
4.	Oxides. Ferric acid	H_2FeO_4	FeO_2Ho_2	122		Fe=45·90
5.	Chlorides. Ferrous chloride (protochloride)	$FeCl_2$	**Fe**″Cl_2	127	2·528; Crystals, 1·926	Fe=44·09
6.	Chlorides. Ferric chloride (per- or sesquichloride)	Fe_2Cl_6	**Fe**‴Cl_3 **Fe**‴Cl_3	325		Fe=34·46
7.	Chlorides. (Bromides and Fluorides similar to Chlorides) ..	$FeBr_2$ and Fe_2Br_6 FeF_2 and Fe_2F_6				
8.	Ferrous iodide	$FeI_2,4H_2O$	**Fe**″I_2	310	2·873	Fe=18·06
9.	Nitrides of iron	Fe_4N_2 Fe_3N		252 182		
10.	Sulphides. Ferrous sulphide (protosulphide)	FeS	**Fe**S	88		Fe=63·63
11.	Sulphides. Ferric disulphide (bisulphide)	FeS_2	**Fe**S_2	120	4·98	Fe=46·66
12.	Sulphides. Other sulphides	Fe_2S_2(?) Fe_2S_3 Fe_3S_4 Fe_7S_8 FeSAs (Mispickel)	'Fe'$_2S_2$	176 208 296 648	4·65 6·13	
13.	Nitrates. Sulphates. Ferrous sulphate (protosulphate)	$FeSO_4,7H_2O$	SOHo$_2$Feo″,6OH$_2$	152	1·857	25·90
14.	Nitrates. Sulphates. Ferric sulphate (persulphate)	Fe'''_23SO_4	$S_3O_6Fe_2o^{vi}$	400		Fe=28·00
15.	Nitrates. Ferrous nitrate	$Fe2NO_36H_2O$	**N**O$_2$Feo″,6OH$_2$ **N**O$_2$	180		Fe=31·11
16.	Nitrates. Ferric nitrate	$Fe'''_26NO_3,12H_2O$				
17.	Carbonates. Ferrous carbonate (protocarbonate)	$FeCO_3$	COFeo″	116		62·07
18.	Ferrous hydric phosphate	$Fe''HPO_4$				
19.	Ferric phosphate	$Fe'''_2P_2O_8,4H_2O$	$P_2O_2Fe_2o^{vi},4OH_2$	302		Fe=37·08
20.	Ferrous oxalate	$2FeC_2O_43H_2O$	CO COFeo″,3OH$_2$	144		Fe=38·88

Compounds of Iron with Oxygen (O).

Ferrous oxide	FeO.
Ferric oxide	Fe_2O_3.
Magnetic or black oxide of iron ...	Fe_3O_4.
Ferric acid	H_2FeO_4.

(1.) Ferrous Oxide.—*Protoxide of iron* (FeO). This body is almost unknown in the free state.

Preparation (as a hydrate, FeH_2O_2). By precipitating a solution of a ferrous salt with an alkali, care being taken that the water in which the ferrous salt is dissolved is entirely free from air.

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Properties.—The white hydrated ferrous oxide rapidly absorbs oxygen from the air, becoming the green hydrate of the magnetic oxide, and finally the brown hydrated peroxide. It is a powerful base, forming *ferrous salts* (*protosalts of iron*). These salts are of a green color, and rapidly oxidize when exposed to the air. It is used to stain glass a green color.

(2.) **Ferric Oxide.**—*Red oxide; Sesquioxide* or *peroxide of iron* (Fe_2O_3), (*colcothar; jeweller's rouge; Venetian red; crocus of Mars;* etc.). It is found native as *hæmatite, specular iron, bloodstone,* etc.

Preparation (anhydrous).—(1.) By the ignition of ferrous sulphate ($2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$).

(2.) (As a hydrate, $Fe_2O_3, 3H_2O$). By acting on a solution of ferric chloride with an excess of ammonia.

Properties.—The hydrate is soluble in acids. When dried and heated to 608° F. (320° C.) it parts with its water, and forms Fe_2O_3. If this be heated to redness it exhibits a sudden glow, contracts in bulk, and, although its composition remains unaltered (the change being molecular), it becomes insoluble in acids. Heated to whiteness oxygen is evolved, and a magnetic oxide formed ($3Fe_2O_3 = 2Fe_3O_4 + O$). With acids it forms *ferric salts* (*persalts of iron*), which are non-crystalline and deliquescent, of a reddish colour, having an astringent taste and an acid reaction.

Like alumina, with which it is isomorphous, it can, although in a lesser degree, act the part of a feeble acid to strong bases, as, *e. g.*, in the compound $4CaO, Fe_2O_3$.

Uses.—Ferric oxide is found in all soils. It serves as a carrier of air to organic matter, whereby CO_2 is prepared for the plant. The ferrous oxide thus formed is again oxidized to ferric oxide, and so fitted once more to perform the same process. The hydrated ferric oxide is largely used as a means of purifying coal-gas from sulphuretted hydrogen, $(Fe_2O_3, H_2O) + 3H_2S = (Fe_2S_3, H_2O) + 3H_2O$. The hydrated ferric sulphide formed is oxidized ("revivified") by exposure to air, considerable heat accompanying the process ($2FeS_3, H_2O + 3O_2 = 2Fe_2O_3, H_2O + 3S_2$). The ferric oxide thus reproduced may be again and again employed, until the free sulphur formed has accumulated in such quantity as to impair the power of the oxide to absorb the gas.

(3.) **Magnetic Oxide of Iron.**—*Black oxide* (Fe_3O_4 or FeO, Fe_2O_3). The latter formula is believed to be the correct one, minerals being known which have the same crystalline form, but where the iron is displaced by other metals, *e. g.*, spinelle (MgO, Al_2O_3). It occurs native as loadstone, and is the chief constituent of the black scales falling from the anvil during the working of wrought iron.

Preparation.—(1) By burning iron in oxygen; (2) By passing steam over hot iron filings; (3) By boiling freshly precipitated hydrated ferric oxide with an excess of iron turnings in water.

(4.) As *a hydrate*, by adding ammonia to a mixture of equivalent parts of ferrous and ferric sulphate, and boiling.

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Properties.—The black oxide is fusible at high temperatures. It is soluble in nitric and in hydrochloric acids; but it does not form definite salts with acids, but simply mixtures of ferrous and ferric salts.

(4.) **Ferric Acid** (H_2FeO_4) exists only in combination as ferrates. A potassic ferrate solution (K_2FeO_4) is prepared either by dissolving in water an ignited mixture of ferric oxide and nitre, or by passing chlorine through a solution of potash (30 parts of KHO in 50 parts of H_2O) in which 1 part of freshly-precipitated hydrated ferric oxide is suspended ($Fe_2O_3+3Cl_2+10KHO=6KCl+2K_2FeO_4+5H_2O$). It is very soluble in water, but is insoluble in a strong potash solution. Its aqueous solution has a fine purple color. It rapidly decomposes ($2K_2FeO_4=2K_2O+Fe_2O_3+3O$), oxygen being evolved and ferric oxide precipitated. The presence of organic matter or the application of heat decomposes it immediately.

COMPOUNDS OF IRON AND CHLORINE.

Ferrous chloride	$FeCl_2$.
Ferric chloride	Fe_2Cl_6.

(5.) **Ferrous Chloride,** *Protochloride of iron* ($FeCl_2$).

Preparation.—(1.) By passing dry hydrochloric acid gas over red-hot iron ($Fe+2HCl=FeCl_2+H_2$).

(2.) By heating ferric chloride in hydrogen ($Fe_2Cl_6+H_2=2FeCl_2+2HCl$).

(3.) (As a *hydrate,* crystals=$FeCl_2$, $4H_2O$). By dissolving iron in hydrochloric acid.

Properties.—The crystals are deliquescent, of a green color, and very soluble in water and in alcohol. By heating in air they are decomposed into Fe_2O_3 and Cl. They rapidly oxidize, even by mere exposure to air.

(6.) **Ferric Chloride;** *Perchloride, Sesquichloride,* or *Trichloride of Iron* (Fe_2Cl_6).

Preparation.—(1.) (*Anhydrous,* Fe_2Cl_6). By the action of chlorine on red-hot iron.

(2.) (As a *hydrate,* $Fe_2Cl_6,6H_2O$). By dissolving ferric oxide in hydrochloric acid.

(3.) By passing chlorine through a solution of ferrous chloride.

Properties.—The *anhydrous* salt is very deliquescent, and rapidly combines with water, its solution becoming red. The *hydrate* is a *red* crystalline body, decomposed by heat into Fe_2O_3 and HCl. Hence the anhydrous salt cannot be prepared from the hydrate. It forms a double salt with ammonic chloride.

Uses.—In solution it is used as a disinfectant, on account of the ease with which it yields chlorine to organic matter, becoming itself reduced to ferrous chloride. It is used in *medicine* and in the *laboratory.* Its solution freely dissolves freshly precipitated ferric hydrate, forming ferric oxychloride.

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(8.) Ferrous Iodide (FeI_2).

Preparation. By digesting iron and iodine in water.

Properties.—It decomposes by exposure to air, and is hence commonly prescribed in medicine in the form of a syrup, by which means its oxidation is retarded.

(10.) Ferrous Sulphide; *Protosulphide* or *sulphide of iron* (FeS).

Preparation. (1.) (*Anhydrous*). By the contact of sulphur with white-hot iron.

(2.) (As a *hydrate.*) By precipitating a ferrous salt with an alkaline sulph-hydrate ($2KHS + FeSO_4 + H_2O = FeS,H_2O + H_2S + K_2SO_4$).

Properties.—The anhydrous compound is insoluble in water and in the alkalies, but is soluble in dilute sulphuric or hydrochloric acids, H_2S being evolved. When heated in the air it first becomes $FeSO_4$, this compound being itself decomposed at a higher temperature. The hydrate rapidly absorbs oxygen when exposed to the air, forming the the red ferric oxide and free sulphur.

(11.) Ferric Disulphide (FeS_2) is found native in all rocks as pyrites (mundic), and is probably formed by the deoxidation of ferrous sulphate by organic matter. By exposure to air some varieties (such as *marcasite*) rapidly absorb oxygen, forming ferrous sulphate. It is a hard body not attracted by the magnet. It is not acted on either by cold sulphuric or by hydrochloric acids. By heat sulphur is driven off, and magnetic pyrites (Fe_3S_4) formed. On account of this property, iron pyrites is largely used in the manufacture of sulphuric acid. (*See* page 152.)

Iron Oxy-Salts.

(13.) Ferrous Sulphate.—*Protosulphate of iron; copperas: green vitriol; iron vitriol* ($FeSO_4$).

Preparation.—(1.) By acting on iron with dilute sulphuric acid and crystallizing ($FeSO_4,7H_2O$). [Other hydrates of $FeSO_4$ have also been obtained].

(2.) By the oxidation of iron pyrites (FeS_2) by contact with air and moisture. (*See* above).

Properties. — A green efflorescent, crystalline (rhomboidal) salt, soluble in alcohol and in water (1 in 2 aq. at 60° F.; 3·7 in 1 aq. at 194° F.; 3·3 in 1 aq. at 212° F.). At a moderate heat the salt becomes white, losing at the same time six molecules of its water. At 500° F. (260° C.) the seventh molecule of water escapes, whilst at a red heat the salt itself is decomposed ($2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$). The preparation of *Nordhausen sulphuric acid* from ferrous sulphate, depends on the circumstance that it is practically impossible to render the sulphate in large bulk perfectly anhydrous, and that therefore the little water remaining in the salt distils over along with the SO_3. The residue (Fe_2O_3) left in the retort when the process is complete is called colcothar.

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By exposing a solution of the salt to air, a brown liquid results, due to the formation of a normal and basic ferric sulphate; the former remaining in solution and the latter being precipitated ($10FeSO_4+O_5 = 3(Fe_2O_3,3SO_3)+2Fe_2O_3,SO_3$). A similar result occurs by the exposure of the solid crystals to air. The aqueous solution of the salt rapidly absorbs nitric oxide. It forms double salts (isomorphous with the magnesic salts), with potassic and ammonic sulphate.

Uses.—In the *laboratory* it is used as a reducing agent, as, *e.g.*, to precipitate metallic gold from its solutions. In *the arts* it is used in the manufacture of black dyes and of ink, by the action of tannic acid infusions upon it.

(14.) **Ferric Sulphate.** — *Persulphate* or *sesquisulphate of iron* ($Fe'''_2 3SO_4$), is found native in Chili, as coquimbite ($Fe_2 3SO_4, 9H_2O$).

Preparation. — By adding the necessary quantity of H_2SO_4 to $Fe''SO_4$ to convert it into $Fe_2 3SO_4$. The mixture is then boiled, the iron being afterwards peroxided by the cautious addition of nitric acid.

Properties.—A non-crystalline, yellow body.

(15.) **Ferrous Nitrate** ($Fe2NO_3, 6H_2O$) is prepared by the action of cold dilute nitric acid on ferrous sulphide; whilst

(16.) **Ferric Nitrate** ($Fe'''_2 6NO_3, 12H_2O$) is prepared by the action of nitric acid (specific gravity 1·2) on metallic iron.

[N.B.—Fuming Nitric Acid (specific gravity 1·5) has no action on iron. (*See* Passive Iron, p. 352.)

(17.) **Ferrous Carbonate,** *Protocarbonate of iron* ($FeCO_3$), is found native as spathic iron ore, and as clay iron ore. It is the iron salt commonly found in mineral waters, retained in solution by the carbonic acid dissolved in the water, from which it is precipitated by the action of oxygen, as a red rusty deposit of hydrated ferric oxide. This deposit is frequently seen on the ground in the neighbourhood of chalybeate springs.

Preparation.—By mixing together solutions of an alkaline carbonate and a ferrous salt.

Properties.—The hydrate formed as above, is a white body, evolving CO_2 and absorbing O (becoming $2FeO_3, 3H_2O$) by mere exposure to air.

(20.) **The Iron Oxalates** are found native (Humboldtite or iron-resin), and may also be produced as lemon-yellow precipitates, by precipitating ferrous sulphate with ammonic oxalate.

Tests.—(*See* Analytical Tables).

CHROMIUM (Cr).

Atomic weight, 52·5. *Specific gravity*, 7·01. *Atomicity; dyad, tetrad, and hexad, also a pseudo-triad and octad* (CrO, CrO_3).

History.—Obtained by Vauquelin (1797), from lead chromate.

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Natural History.—It is found as chrome-iron-slate (FeO,Cr_2O_3), and also as lead-chromate ($PbCrO_4$).

Preparation.—(1.) By heating the oxide with charcoal.

(2.) By the action of metallic-sodium or potassium on chromic chloride.

Properties.—(*a.*) *Physical.* A hard, crystalline (octahedra), highly infusible metal.

(*β.*) *Chemical.*—It is not oxidized by heating in the open air. It is not acted on by any acid except hydrofluoric acid, but is converted into a chromate by ignition with the hydrated alkalies.

Compounds of Chromium.

Atomic Weight, Cr 52.

		COMPOUNDS.	Formula (Common).	Formula (Constitutional).	Molecular Weight.	Specific Gravity.	Cr per cent.
1.	Oxides.	Chromous oxide (protoxide)..	CrO	$\mathbf{Cr}O$	68·0		76·47
2.	Oxides.	Chromic oxide (sesquioxide)..	Cr_2O_3	$\left\{\begin{matrix}\mathbf{Cr}O\\O\\\mathbf{Cr}O\end{matrix}\right.$	152·0	5·21	68·42
3.	Oxides.	Chromous dichromic tetroxide	CrO,Cr_2O_3	$\left\{\begin{matrix}\mathbf{Cr}O\\\mathbf{Cr}O\end{matrix}\right.Cro''$	220·0		70·90
4.	Oxides.	Chromic dioxide	CrO_2				
5.	Oxides.	Chromic anhydride	CrO_3	$\mathbf{Cr}^{vi}O_3$	100·0	2·676	52·00
6.	Chromates.	Potassic chromate	K_2CrO_4	$\mathbf{Cr}O_3Ko_2$	194·2	2·682	26·77
7.	Chromates.	Potassic dichromate	$K_2Cr_2O_7$	$\mathbf{Cr}_2O_5Ko_2$	294·2	2·624	35·35
8.	Chromates.	Potassic trichromate	$K_2Cr_3O_{10}$	$\mathbf{Cr}_3O_8Ko_2$	394·2		39·57
9.	Chromates.	Potassic tetrachromate ..	$K_2Cr_4O_{13}$	$\mathbf{Cr}_4O_{11}Ko_2$	494·2		42·08
10.	Chromates.	Sodic chromate	$Na_2CrO,10H_2O$	$\mathbf{Cr}O_2Nao_2$	162·0		32·09
11.	Chromates.	Hydric sodic chromate ..	$2(NaHCrO_4),H_2O$				
12.	Chromates.	Ammonic dichromate	$(NH_4)_22CrO_3$				
13.	Chromates.	Baric chromate	$BaCrO_4$	$\mathbf{Cr}O_2Bao''$	253·0		20·55
14.	Chromates.	Plumbic chromate	$PbCrO_4$	$\mathbf{Cr}O_2Pbo''$	323·0	5·653	16·09
15.	Chromates.	Basic plumbic chromate ..	$2PbO,CrO_3$			6·266	
16.	Chromates.	Argentic chromate..	Ag_2CrO_4	$\mathbf{Cr}O_2Ago_2$		5·77	23·21
17.	Chromates.	Argentic dichromate	$Ag_2O,2CrO_3$				
18.	Chlorides.	Chromous chloride..	$CrCl_2$	$\mathbf{Cr}Cl_2$	123·0		42·27
19.	Chlorides.	Chromic chloride (sesquichloride)..	Cr_2Cl_6	$\left\{\begin{matrix}'\mathbf{Cr}'''Cl_3\\'\mathbf{Cr}'''Cl_3\end{matrix}\right.$	317·0		32·80
20.	Chlorides.	Chromic oxy-dichloride (chlorochromic acid)	$CrCl_2O_2$	$\mathbf{Cr}O_2Cl_2$	155·0	1·92	33·54
21.		Chromic sulphide	Cr_2S_3		200·0		52·00
22.		Chromic sulphate	Cr_23SO_4	$\mathbf{S}_3O_6Cr_2o^{vi}$	392·0		26·53
23.		Chromic nitrate	Cr_26NO_3				

(1.) **Chromous Oxide** (CrO) is only known as a hydrate (CrH_2O_2), It is produced by adding potassic hydrate to a solution of chromous chloride. It absorbs oxygen with great energy, forming CrO,Cr_2O_3. It is a feeble base.

(2.) **Chromic Oxide.**—*Sesquioxide of chromium* (Cr_2O_3).

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Preparation.—If a solution of potassic dichromate, acidulated with sulphuric acid, be boiled with alcohol, or if a current of SO_2 be passed through a solution of the dichromate, the chromic acid loses half its oxygen, and a chromic sulphate is formed. On adding ammonia to this solution, the hydrated sesquioxide ($Cr_2H_6O_6$) is precipitated, which on ignition leaves Cr_2O_3.

Properties.—Chromic oxide has a brilliant green color, which is unaffected by heat, and is, consequently, largely used in enamel painting. It constitutes the green coloring matter of the emerald. "*Guignet's green*" has the composition $Cr_4H_6O_9$.

The hydrate forms two sets of salts with acids, one of which is green and non-crystalline, and the other violet and crystalline.

The anhydrous sesquioxide is insoluble in acids.

(3.) **Chromic Anhydride** (Chromic acid) (CrO_3).

Preparation.—By adding an excess of sulphuric acid to a strong solution of potassic bichromate, and crystallizing.

Properties.—Chromic anhydride crystallizes in needle-shaped crystals, which are deliquescent, and soluble in water. It is decomposed by heat with the evolution of oxygen. It is a powerful oxidizing body ($4CrO_3 = 2Cr_2O_3 + 3O_2$), and is used as an agent in bleaching certain oils. Heated with hydrochloric acid, chlorine is liberated; when heated with sulphuric acid, oxygen is set free. The color of the ruby is believed to be due to the presence of a trace of chromic acid.

(4.) **Potassic Chromate** (K_2CrO_4).

Preparation.—(1.) By adding potassic carbonate to a solution of potassic dichromate.

(2.) By fusing a chromium compound with potassic carbonate.

(3.) (*See below.*)

Properties.—A yellow crystalline salt, soluble in water (1 in 2 aq. at 60° F.), the solution having an alkaline reaction. It fuses by heat, becoming red without decomposing.

(5.) **Potassic Dichromate** or *anhydrochromate.*—*Bichromate of Potash* ($K_2Cr_2O_7$).

Preparation.—(1.) By the action of sulphuric acid on potassic chromate.

(2.) Commercially the salt is prepared as follows:—Powdered chrome ironstone is heated in air with chalk and potassic carbonate. The ferrous oxide is thus changed into the insoluble ferric oxide, and the chromic oxide (Cr_2O_3) into chromic acid (CrO_3), which forms, with the potash, potassic chromate (K_2CrO_4). The mass is then acted on with water, and the clear solution mixed with nitric acid and crystallized:—

$$2(K_2CrO_4) + 2HNO_3 = K_2Cr_2O_7 + 2KNO_3 + H_2O.$$

Potassic chromate + Nitric acid = Potassic dichromate + Potassic nitrate + Water.

Properties.—A red crystalline salt. It fuses at a moderate heat, but

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is decomposed when the heat approaches redness, with the evolution of oxygen. It is soluble in water (1 in 10 aq. at 60° F.).

(12.) Plumbic Chromate.—*Chromate of lead; Chrome yellow* ($PbCrO_4$). This body is found native as red lead ore (Siberia).

Preparation.—By the action of lead acetate on potassic chromate.

Properties.—A yellow poisonous pigment. When heated it turns brown, and evolves oxygen ($8PbCrO_4 = 4(PbCrO_4,PbO) + 2Cr_2O_3 + 3O_2$). It is insoluble in water and in acids, but is soluble in an excess of potassic hydrate.

Uses.—In the *arts* it is used as a yellow pigment, and in the *laboratory* as a source of oxygen in organic combustion analysis.

(13.) Basic Plumbic Chromate.—*Orange chrome* ($2PbO,CrO_3$).

Preparation.—By boiling together lime and plumbic chromate :—

$$2(PbO,CrO_3) + CaO = 2PbO,CrO_3 + CaCrO_4.$$

Plumbic carbonate + Lime = Basic plumbic chromate + Calcic chromate.

Properties.—A scarlet pigment. It is used in calico printing, the fabric being first dyed with plumbic chromate and afterwards boiled in lime-water.

(16.) Chromous Chloride ($CrCl_2$).

Preparation.—By heating chromic chloride in a current of dry hydrogen.

Properties.—A white substance, the aqueous solution of which is blue, but becomes green by exposure to air. It is a powerful reducing agent.

(17.) Chromic Chloride.—*Sesquichloride of chromium* (Cr_2Cl_6).

Preparation—(1.) (*Anhydrous.*) By passing dry chlorine over a heated mixture of chromic oxide and charcoal. The Cr_2Cl_6 collects as a violet sublimate in the cool part of the tube.

(2.) (*As a hydrate*).—(*a*) By dissolving chromic hydrate in hydrochloric acid; or (*β*) by boiling either chromic acid, or the lead or silver chromate, with hydrochloric acid and some reducing agent such as alcohol, SO_2, etc.

Properties.—Insoluble in acids or in cold or boiling water. If a trace of chromous chloride be added to the salt suspended in water, it becomes soluble, great heat being evolved in the act of solution.

The **Fluorides of Chromium** (CrF_6 and Cr_2F_6) have been prepared.

(18.) Chromic Oxydichloride.—*Chlorochromic acid* ($CrCl_2O_2$).

Preparation.—By distilling sulphuric acid with a fused mixture of common salt and hydric potassic chromate :—

$$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 = K_2SO_4 + 2Na_2SO_4 + 3H_2O + 2CrCl_2O_2.$$

Properties.—A red liquid (Sp. Gr. 1·92) emitting suffocating red fumes (Sp. Gr. of vapor, 5·52). It catches fire when dropped into

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alcohol, or into a solution of ammonia. It is decomposed by water.

(19.) Chromic Sesquisulphide (Cr_2S_3) has been obtained. Chromium, however, has but little affinity for sulphur.

(20.) Chromic Sulphate ($Cr_2 3SO_4$).—There are three varieties of chromic sulphates:—

(α.) A *green* sulphate ($Cr_2 3SO_4, 5H_2O$), which is soluble in alcohol and is non-crystalline. It is prepared either (α) by boiling hydrated chromic oxide with sulphuric acid, or (β) by boiling a solution of the violet sulphate, or (γ) by heating the crystals of the violet sulphate to 212° F. (100° C.).

(β.) A *violet* sulphate ($Cr_2 3SO_4, 15H_2O$), which is insoluble in alcohol and is crystalline. It is prepared by digesting the dried hydrated sesquioxide with sulphuric acid at ordinary temperatures. With potassic sulphate it forms chrome alum ($K_2Cr_2 4SO_4, 24H_2O$, Sp. Gr. 1·826).

(γ.) A *red* sulphate ($Cr_2 3SO_4$). A crystalline salt, insoluble either in alcohol, in water, or in acids (even in aqua regia). It is prepared by heating the green or the red variety to 698° F. (370° C.).

Tests.—(*See* ANALYTICAL TABLES.)

TITANIUM (Ti).

Atomic weight, 50. *Specific gravity*, 5·3. *Atomicity dyad and tetrad* (TiO; $TiCl_4$).

History.—Discovered by Gregor (1791).

Natural History.—It is never found free, but occurs in titaniferous iron (as in *iron sand*); also as titanic anhydride (TiO_2), in rutile, anatase, Brookite, etc.

Prepapation.—(1.) By heating titanic oxide (TiO_2) with charcoal.
(2.) By heating sodium in the vapor of titanic chloride.

Properties.—A dark green substance. It burns with vivid scintillations in air and oxygen, and in burning absorbs both oxygen and nitrogen. Hydrochloric acid dissolves it, with the evolution of hydrogen. It has a great affinity for nitrogen. If a mixture of charcoal and titanic anhydride be heated, and whilst hot introduced into a jar of nitrogen, the nitrogen will be absorbed, and CO be formed. If ammonia gas be passed over red-hot titanic anhydride, the violet titanium dinitride (TiN_2) is formed; or if ammonia be passed over $4H_3N, TiCl_4$, the nitride Ti_3N_4 results.

In iron furnaces certain crystals are frequently found adhering to the slag, which consist of a mixture of cyanide and nitride of titanium ($TiCy_2, 3Ti_3N_2$) (Wöhler). They are extremely hard, almost absolutely infusible, and have a specific gravity of 5·3. They are insoluble in any acid, except in a mixture of nitric and hydrofluoric acids.

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Compounds of Titanium.

	NAMES.	Formula (Common.)	Formula (Constitutional.)	Molecular Weight.	Specific Gravity.	Ti per cent.
1.	Titanous oxide—Protoxide of titanium	TiO	TiO	66		75·75
2.	Sesquioxide of titanium ..	Ti_2O_3		148		
3.	Titanic oxide or anhydride	TiO_2	TiO_2	82		60·97
4.	Titanic acid	TiO_2H_2O	$TiOHo_2$	100		50·00
5.	Dititanic hexachloride ..	Ti_2Cl_6	$TiCl_3$ $TiCl_3$	313		31·95
6.	Titanic chloride (tetrachloride)	$TiCl_4$	$TiCl_4$	192	1·760	26·04
7.	Dititanic hexafluoride ..	Ti_2F_6	TiF_3 TiF_3	214		46·72
8.	Titanic fluoride	TiF_4	TiF_4	126		39·68
9.	Titanic sulphide	TiS''_2	TiS''_2	114		43·86
10.	Dititanic dinitride	Ti_2N_2	TiN''' TiN'''	128		78·12
11.	Trititanic tetranitride ..	$Ti_3N'''_4$		206		72·81

Oxides. Chlorides. Fluorides.

Compounds of Titanium and Oxygen.

Titanous oxide ... . TiO.
Sesquioxide of titanium ... ... Ti_2O_3.
Titanic oxide ... ... TiO_2.

(1.) Titanous Oxide.—*Protoxide of titanium* (TiO) is a black powder, and may be obtained by heating TiO_2 in a crucible lined with charcoal (?).

(2.) Sesquioxide of Titanium (Ti_2O_3) is obtained as a dark brown precipitate on adding ammonia to a hydrochloric acid solution of titanic acid after digestion with metallic copper at 122° F. (50°C.). It rapidly absorbs oxygen from the air.

(3.) Titanic Oxide.—*Dioxide; titanic anhydride; titanic acid* (TiO_2). This body occurs native as rutile (*Specific gravity*, 4·25. *Crystals, brown needle-prisms*), anatase (*Specific gravity*, 3·9. *Crystals, blue transparent octahedra*), and Brookite (*Specific gravity*, 4·13. *Crystals, right rhombic prisms*). It also occurs in combination with oxide of iron (iron sand).

Preparation.—Powdered "rutile," or "iron sand," is first fused with potassic carbonate. After the fused mass has been treated with hot water, the residue (an acid potassic titanate) is dissolved in hydrochloric acid, and the solution evaporated to dryness. In this way the titanic oxide and any silica present are converted into insoluble modifications. This residue is now fused with acid potassic sulphate, whereby a yellow mass is obtained having the composition TiO_2,SO_3, and which, being soluble, may be separated from the silica by treat-

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ment with cold water. On boiling the solution, the titanic oxide is precipitated as a white powder. By continuous heating this white powder becomes anhydrous, its color changing to *black*, its specific gravity likewise increasing. It moreover becomes insoluble in all acids, except in hydrofluoric and in boiling sulphuric acids. Fused with potash, it forms a yellow potassic titanate, which is soluble in hydrochloric acid, from which solution titanic oxide may be precipitated as a hydrate on adding ammonic carbonate.

Titanic oxide (*hydrate*) is yellow when hot and white when cold. It is soluble in hydrochloric and sulphuric acids (thus distinguishing it from silica). It is insoluble in a solution of potassic hydrate, but forms a titanate when fused with potash. The potassic titanate is decomposed by water, an acid potassic titanate being formed which is soluble in hydrochloric acid, from which solution hydrated titanic acid ($TiO_{21}H_2O$) may be precipitated by ammonia.

The titanates may be represented either as $2M'_2O,TiO_2(=M'_4TiO_4)$, or as $M'_2O,TiO_2(=M_2TiO_3)$.

Compounds of Titanium and Chlorine.

Titanous chloride...	$TiCl_3$.
Titanic chloride	$TiCl_4$.

(4.) **Titanous Chloride** ($TiCl_3$) forms lustrous violet-colored crystals, prepared by heating titanic chloride in hydrogen.

(5.) **Titanic Chloride.**—*Tetrachloride of titanium* ($TiCl_4$) is prepared by passing chlorine over a red-hot mixture of titanic oxide and charcoal. It is a volatile colorless liquid (Specific gravity of vapor, 6·836; of liquid, 1·761, at 32° F.) It boils at 275° F. (135° C.). It is decomposed by an excess of water.

Reaction of Titanium Compounds.

(A.) *Titanous compounds.*

Ammonic Carbonate.—A blue ppt., changing to brown and then to green.

(B.) *Titanic compounds* (titanic acid dissolved in HCl).

(1.) *Ammonia,* a white ppt.

(2.) *Infusion of galls,* an orange-coloured ppt.

(3.) *Potassic ferrocyanide,* a brown ppt.

(4.) The *borax bead,* or *microcosmic* salt, gives in the inner blowpipe flame a yellow bead when hot, which changes to violet as it cools.

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CHAPTER XVI.

METALS OF GROUP II.

A.—Metals whose Sulphides are Insoluble in the Alkaline Sulphides.

Copper and its Componnds—Bismuth and its Compounds—Cadmium—Compounds with Oxygen, with the Haloids, and with Sulphur — Palladium and its Compounds—Rhodium and its Compounds—Osmium and its Compounds—Ruthenium and its Compounds.

B.—Metals whose Sulphides are Soluble in the Alkaline Sulphides.

Tin and its Compounds—Antimony and its Compounds—Arsenic and its Compounds — Gold and its Compounds — Platinum and its Compounds — Bases produced by the action of Ammonia on the Chlorides of Platinum—Molybdenum and its Compounds.

COPPER (Cu″=63·4).

Atomic weight and Molecular weight, 63·4. *Specific Gravity*, 8·9. *Fuses*, 1996° F. (1091° C.). *Atomicity, dyad, as in Cupric Salts*, $Cu''Cl_2$; *Pseudo-monad as in Cuprous Salts*, (Cu'_2Cl_2).

Natural History.—Copper is found native both in masses and in crystals, not unfrequently associated with silver. The common copper ores are a sulphide of copper and iron, called "copper pyrites," or "yellow copper ore" (Cu_2S,Fe_2S_3), a cuprous sulphide, or "copper glance" (Cu_2S), a cuprous oxide or "red copper ore," or "ruby ore" (Cu_2O). Copper is also found as cupric oxide or "black oxide" (CuO), and as malachite, the green malachite having the composition represented by the formula ($CuCO_3,CuO,H_2O$), and the blue malachite ($2CuCO_3,CuO,H_2O$).

Preparation.—*From copper pyrites* (Cu_2S,Fe_2S_3) (Copper smelting). The ore is sorted, that is, those pieces rich in copper are picked out and broken up, whilst the part less rich in metal is powdered and sifted.

(1.) *Calcination of ore.*—The ore is first *calcined* or *roasted*, whereby the arsenic and part of the sulphur are volatilized as As_2O_3 and SO_2, cuprous sulphide with some oxide, and ferric oxide (converted from the ferric sulphide) with some sulphide, remaining. The ferric sulphide is far more easily oxidised than the cuprous sulphide. Hence the chief part of the Cu_2S remains unaltered.

[The fumes given off during roasting are called "*copper smoke*,"

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and contain As, As_2O_3, SO_3, SO_2, and HF, the latter being derived from the fluor spar contained in the ore.]

(2.) *Fusion for coarse metal.*—The calcined ore is now mixed with sand, and with a slag containing a quantity of silicate, fluor spar being added if necessary, to increase the fluidity of the slag. The mixture is now intensely heated in the "ore furnace." The following changes occur:—The cuprous oxide acts on the ferric sulphide present, cuprous sulphide and ferric oxide being formed. But inasmuch as there is more ferric sulphide in the ore than can be oxidized by the cuprous oxide present, the excess of the fused ferric sulphide, together with the cuprous sulphide, sink to the bottom of the furnace to form what is called the "*mat*" or "*coarse metal*" ($=CuFeS_2$). This coarse metal is granulated by being run off into water whilst in a liquid state.

The ferric oxide present combines with the silica to form a fusible slag (silicate of iron) ($FeSiO_3$), which is used for building purposes.

(3.) *Calcination of the coarse metal.*—The coarse metal is now calcined, whereby any sulphide of iron present is converted into oxide.

(4.) *Fusion for white metal.*—The roasted coarse metal is now fused with silica, and with an ore rich in cupric oxide, whereby any unchanged iron sulphide is converted into oxide. The whole of the iron which is now present as ferric oxide combines with the silica to form a fusible slag, the "mat," or "regulus of white metal," or the "*fine metal*," as it is now called, being nearly pure cuprous sulphide (Cu_2S).

Sometimes the roasting is carried further, so that a portion of the Cu_2S becomes reduced. This reduced portion sinks to the bottom, along with most of the foreign metals present, these parting with their sulphur more readily than the copper. Hence the *upper* part of the ingot is always the purest, and is known as "*best selected copper*," whilst the *under* portion, containing the impurities, is known as "*tile copper*."

(5.) *Roasting for blistered copper.*—The fine metal (Cu_2S) is now roasted, whereby some of the copper becomes converted into CuO, the sulphur escaping as SO_2. Hence the mass after roasting consists of Cu_2S and CuO. The temperature is now raised, when mutual decomposition occurs between the cuprous sulphide and the cupric oxide, metallic copper and sulphurous anhydride (which escapes) being formed ($Cu_2S+2CuO=SO_2+4Cu$). This copper is called "*pimple*," or "*blistered copper*," blisters being formed upon it, by the escape of the last portions of the SO_2.

(6.) *Refining.*—This is effected by melting the copper, so as to oxidise the last traces of sulphur and of foreign metals, such as Fe, Sn, Pb, etc., present. Some cuprous oxide (Cu_2O) is produced during the process, a part of which forms a slag with any sand present, whilst

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another part is dissolved by the metallic copper. The presence of this cuprous oxide in copper renders the metal brittle ("*dry copper*").

(7.) *Toughening* (*poling*).—After the removal of the slag, some anthracite is thrown on the surface of the melted metal, to prevent it becoming further oxidised. It is then well stirred with a pole of young wood (*poled*), the combustible gases given off by the wood, burning at the expense of any oxide present in the liquid metal. The presence of a little suboxide in the metal is said to render it tough. Hence "over-poling" (that is when the whole of the cuprous oxide is removed), or "under-poling" (that is where too much is left), are both to be avoided. When the copper is properly poled it is known as "tough cake."

In the preparation of copper from the oxide, or from the carbonate, all that is necessary is to reduce a mixture of the copper salt with carbon and silica, in a wind furnace.

A pure copper may be obtained by electrolysis, or by heating the oxide in a current of hydrogen.

Impurities.—Sulphur (which injures the malleability of the copper), arsenic, phosphorus (which increases its hardness), tin, antimony, nickel, bismuth, silver, and selenium, are the ordinary impurities.

Properties.—(*α.*) *Physical.* A red metal, having a metallic taste and a peculiar smell. It is found native, and may be prepared artificially both in cubes and in octahedra. It is very heavy (Sp. Gr. 8·9), hard, ductile, malleable, and sonorous. It fuses at 1996° F. (1091° C.), and at a white heat is said to be slightly volatile. It is a good conductor both of heat and electricity.

(*β.*) *Chemical.*—Copper is not affected by air, dry or moist, at ordinary temperatures, but it oxidises rapidly in air at a red heat, black scales of cupric oxide (CuO) pealing off from the surface of the metal. When finely divided it burns like tinder. In the oxyhydrogen blowpipe the metal burns, rendering the flame green. It is unacted upon by pure water, nor indeed has a current of steam any action on the red-hot metal. When placed in solutions of chlorides, as in *sea-water*, copper becomes coated with the green *oxychloride* ($CuCl_2,3CuO,4H_2O$). Copper vessels are, therefore, dangerous for culinary purposes, inasmuch as a certain quantity of the metal is certain to be dissolved when solutions of common salt or acids (such as vinegar, rhubarb, etc.), or liquids containing fatty and oily matters, are boiled in contact with the metal.

Nitric acid and boiling sulphuric acid dissolve it. With the former nitric oxide (N_2O_2) is evolved, and with the latter sulphurous anhydride (SO_2). Liquid hydrochloric acid acts upon the metal when finely divided, evolving hydrogen. When a current of hydrochloric acid gas is passed over the red-hot metal, hydrogen is set free, and cuprous chloride (Cu_2Cl_2) is formed. Ammonia dissolves copper, but the fixed alkalies have very little action upon it. It combines with

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chlorine energetically, thin leaves of metallic copper catching fire as soon as they are exposed to the action of the gas.

Uses.—For coinage; for sheathing ships; for alloys. The composition of certain alloys is stated in the following table, taken from Bloxam.

	Copper.	Zinc.	Tin.	Iron.	Nickel.	Aluminium.
Brass	64·0	36·0				
Muntz metal..	60 to 70	40 to 30				
German silver	51·0	30·5	—	—	18·5	
Aich (or Gedge's) metal	60·0	38·2	—	1·8		
Sterro metal..	55·0	42·4	0·8	1·8		
Bell metal	78·0	—	22·0			
Speculum metal	66·6	—	33·4			
Bronze metal	80·0	4·0	16·0			
Gun metal	90·5	—	9·5			
Bronze coinage	95·0	1·0	4·0			
Aluminium bronze ..	90·0	—	—	—	—	10·0

Compounds of Copper.

	COMPOUNDS.	Formula (General).	Formula (Constitutional).	Molecular Weight, Anhydrous Salts.	Specific Gravity.	Proportion of Cu or CuO in the Salts.
1.	Cuprous hydride	Cu_2H_2	$\left\{\begin{matrix}CuH\\CuH\end{matrix}\right.$	128·8		Cu = 98·44
2.	Cuprous quadrantoxide ..	Cu_4O				
3.	Cuprous oxide (red oxide)..	Cu_2O	$'Cu'_2O$	142·8		Cu = 88·79
4.	Cupric oxide (black oxide)	CuO	CuO	79·4	6·5	Cu = 79·85
5.	Cuprous hydrate	$4Cu_2O,H_2O$	$4'Cu'_2O,OH_2$			
6.	Cupric hydrate	CuH_2O_2	$CuHo_2$			
7.	Cuprous chloride (subchloride)..	Cu_2Cl_2	$'Cu'_2Cl_2$	197·8	3·37	Cu = 64·10
8.	Cupric chloride (chloride)..	$CuCl_2$	$CuCl_2$	134·4	3·05	Cu = 47·17
9.	Hydrated cupric oxychloride of copper..	$CuCl_2,3CuH_2O_2$				
	[Corresponding bromides and iodides have been prepared.]					
0.	Tricupric nitride	Cu_6N_2		408·4		Cu = 93·14
1.	Cuprous sulphide (copper glance)	Cu_2S	$'Cu'_2S''$	158·8	5·5	Cu = 79·84
2.	Cupric sulphide	CuS	CuS''	95·4	3·8	Cu = 66·45
3.	Cupric pentasulphide ..	CuS_5				
4.	Cupric phosphide	Cu_3P_2	$P_2Cu''_3$	252·2		Cu = 75·41
5.	Cupric selenide					
6.	Cupric sulphate (blue vitriol)	$CuSO_4,5H_2O$	$SOHo_2Cuo'',4OH_2$	159·4	2·25	CuO = 31·84
7.	Cupric nitrate	$Cu2NO_3,6H_2O$	$\left\{\begin{matrix}NO_2Cuo''\\NO_2\end{matrix}\right.,4OH_2$	187·4		Cu = 33·83
8.	Hydrated oxy-carbonate of copper (azurite)	$2CuCO_3,CuH_2O_2$	$\left\{\begin{matrix}CHoCuo''\\CHoCuo''\end{matrix}\right.,Cuo''$	344·2	3·8	Cu = 55·22
9.	Hydrated dibasic carbonate (malachite)	$CuCO_3,CuH_2O_2$	$CO(OCuHo)_2$	220·8	3·9	Cu = 57·42
0.	Dicupric carbonate (mysorin)	$2CuO,CO_2$	$CCuo''_2$	202·8		Cu = 62·52

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COMPOUND OF COPPER AND HYDROGEN.

Cuprous hydride ... ... Cu_2H_2.

(1.) Cuprous Hydride (Cu_2H_2)

Preparation.—By heating a cupric sulphate solution with hypophosphorous acid to 140° F. (60° C.).

Properties.—A black powder, evolving hydrogen when heated. It catches fire when exposed to the action of chlorine. Hydrochloric acid forms with it cuprous chloride, the combination being accompanied by the evolution of hydrogen ($Cu_2H_2+2HCl=Cu_2Cl_2+2H_2$)

COMPOUNDS OF COPPER AND OXYGEN.

Cuprous quadrantoxide ... ... Cu_4O.
Cuprous oxide (red oxide) ... ... Cu_2O.
Cupric oxide (black oxide) ... ... CuO.

(2.) Cuprous Quadrantoxide (Cu_4O). This oxide is only known as a green hydrate, and may be prepared by digesting in closed vessels, a cupric salt with an excess of stannous chloride dissolved in a large excess of potassic hydrate.

(3.) Cuprous Oxide, *Suboxide* or *red oxide of copper* (Cu_2O).

Molecular weight=142·8. *Specific gravity*, 5·7. *Found native in octahedral crystals.*

Preparation.—(1.) By boiling grape sugar in a solution of cupric sulphate, containing an excess of potassic hydrate.

(2.) By igniting a mixture of 5 parts of cupric oxide (CuO) and 4 parts of copper filings.

(3.) By boiling a mixed solution of cupric sulphate, sodic sulphite, and sodic carbonate ($2CuSO_4+2Na_2CO_3+Na_2SO_3=Cu_2O+3Na_2SO_4+2CO_2$).

(4.) By acting on an ammoniacal solution of cupric oxide with metallic copper, air being excluded, the *blue* solution of CuO becoming the *colorless* solution of Cu_2O ($Cu+CuO=Cu_2O$).

(5.) *As a hydrate* ($4Cu_2O,H_2O$.) By decomposing cuprous chloride with potassic hydrate.

Properties.—(α.) *Physical.* A reddish-yellow powder.

(β.) *Chemical.* In the moist state it is slowly oxidized by air. It is a feeble base. There are no cuprous oxy-salts (except sulphites and certain double sulphites), the oxy-acids decomposing cuprous oxide, and forming a mixture of a cupric salt and metallic copper. Thus nitric acid converts cuprous oxide into cupric nitrate, and hydrochloric acid into cuprous chloride (Cu_2Cl_2). It is soluble in ammonia, *the solution being colorless*, but in the presence of a mere trace of oxygen the solution turns blue from the formation of cupric oxide.

It is slightly soluble in metallic copper, which it renders what is called "dry" or "brittle."

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Uses.—For stained glass, to which it imparts a fine *red* color.

(5.) **Cupric Oxide;** *Copper monoxide; black oxide of copper* (CuO).

Molecular weight, 79·4. *Specific gravity*, 6·5.

Preparation.—(1.) By heating the metal in air.

(2.) By the ignition of cupric nitrate or carbonate ($2Cu2NO_3 = 2CuO + 2N_2O_4 + O_2$).

(3.) (*As a hydrate*, $Cu_2H_2O_2$). By adding potassic hydrate in excess, to a solution of a cupric salt. The hydrate (blue) becomes anhydrous (black) by boiling in water.

Properties.—(α.) *Physical.* The hydrate (CuH_2O_2) has a light blue color, but the anhydrous compound is black. Heat has no effect upon it. It is insoluble in water, but is soluble in oils and fats. Hence the danger of copper for culinary purposes.

(β.) *Chemical.*—Cupric oxide is a hygroscopic body, absorbing water freely from the air, although not soluble in water. It is soluble in most acids, forming cupric salts that are isomorphous with magnesic salts. It combines when fused with the fixed alkalies. The hydrate is soluble in ammonia water, forming a blue solution, having the property of dissolving cellulose, which cellulose is reprecipitated from the solution by an acid. The blue solution is also formed when copper filings are shaken up in an ammonia solution in the presence of air, a portion of the ammonia becoming oxidised simultaneously with the copper, white fumes of ammonic nitrite being formed. It is decomposed when heated in hydrogen with the evolution of heat and light.

Uses.—In organic combustion analysis to furnish oxygen. It is used to stain glass a fine *green* color.

Compounds of Copper and Chlorine.

Cuprous chloride	Cu_2Cl_2.
Cupric chloride	$CuCl_2$.

(7.) **Cuprous Chloride.**—*Subchloride of copper* (Cu_2Cl_2 or $'Cu'_2Cl_2$). *Molr. Wt.*=197·8. *Specific gravity*, 3·3.

* *Preparation.*—(1.) By the action of hydrochloric acid on copper in the presence of air ($2Cu_2 + 4HCl + O_2 = 2Cu_2Cl_2 + 2H_2O$).

(2.) By distilling one part of copper filings with two parts of mercuric chloride.

(3.) By boiling together cupric chloride and sugar.

(4.) By heating dry cupric chloride in a current of dry ammonia.

(5.) By the action of stannous chloride on a cupric salt ($2CuCl_2 + SnCl_2 = Cu_2Cl_2 + SnCl_4$).

Properties.—(α.) *Physical.* A white compound, turning grey when moistened and exposed to light. It may be obtained in tetrahedral crystals. It fuses when heated to a yellow mass. It is insoluble in water.

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(β.) *Chemical.* Hydrochloric acid dissolves it. The colorless solution thus formed throws down cuprous chloride on the addition of water. The acid solution readily absorbs carbonic oxide, from which solution the crystalline compound ($4Cu_2Cl_2,3CO,7H_2O$) may be obtained. It also absorbs oxygen, when the solution becomes brown and deposits a green cupric oxychloride ($CuCl_2,3CuO,4H_2O$), known as "*Brunswick green.*" This latter substance is also found native (atacamite).

Ammonia solution dissolves it, forming (air being excluded) a colorless liquid. This solution rapidly absorbs oxygen, when it becomes deep blue. It gives a red precipitate with acetylene, for which it constitutes a delicate test. With argentic nitrate it deposits silver, the ammonia holding the silver chloride and copper nitrate in solution $Cu_2Cl_2+4AgNO_3=2(Cu2NO_3)+2AgCl+Ag_2$.

Cuprous chloride is soluble in potassic chloride, forming with it the double salt ($4KCl,Cu_2Cl_2$). It is also soluble in ammonic chloride, white dodecahedral crystals of $Cu_2Cl_2\ (NH_3)_2$ being deposited from the fresh solution, or, if after prolonged exposure to air, blue cubical crystals of $Cu''Cl_2(NH_3)_2,2NH_4Cl$.

(8.) Cupric Chloride.—*Chloride of copper* ($CuCl_2$).

Preparation.—(1.) By dissolving cupric oxide in hydrochloric acid and crystallizing ($=CuCl_2,2H_2O$).

(2.) By the spontaneous combustion of copper in chlorine.

Properties.—Green deliquescent crystals (specific gravity, 2·5), becoming blue when dried. The salt fuses and is decomposed by heat into chlorine and cuprous chloride. It is very soluble both in alcohol and in water, the aqueous solution being green when concentrated and blue when dilute. The spirit solution burns with a green flame. It forms double salts with the alkaline chlorides.

Cuprous Bromide or *subbromide of copper* (Cu_2Br_2) and **Cupric Bromide** ($CuBr_2$), **Cuprous Iodide** or *subiodide of copper* (Cu_2I_2,H_2O), a white insoluble powder, and **Cupric Iodide** (CuI_2), have been prepared.

(10.) Tricupric Nitride (Cu_6N_2).

Preparation.—By passing ammonia gas over cupric oxide heated to 482° F. (250° C.).

The nitride is a dark green powder.

COMPOUNDS OF COPPER AND SULPHUR.

Cuprous sulphide	Cu_2S.
Cupric sulphide	CuS.
Cupric pentasulphide	CuS_5.

(11.) Cuprous Sulphide.—*Subsulphide of copper* (the "fine metal" of the copper smelter) (Cu_2S). This body is found native in six-sided prisms, as "copper glance" or "Redruthite." *Copper pyrites* is a cuprous-ferric-sulphide (Cu_2S,Fe_2S_3).

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Preparation.—By melting together three parts of sulphur and eight of copper.

Properties.—Fusible by heat (Sp. Gr. 5·5). Soluble (with decomposition) in nitric acid and in aqua regia, but insoluble in hydrochloric acid.

(12.) Cupric Sulphide.—*Sulphide of copper* (CuS). Found native as "indigo copper," "blue copper," or "covellin."

Preparation.—(As a hydrate.) By precipitating cupric salts with sulphuretted hydrogen.

Properties.—The hydrated cupric sulphide, by exposure to air, rapidly becomes sulphate. It is soluble in nitric acid.

(13.) Cupric Pentasulphide (CuS_5).

Preparation.—By decomposing a cupric salt with an alkaline pentasulphide.

Properties.—A black precipitate, insoluble in potassic carbonate.

(14.) Cupric Phosphide.—*Phosphide of copper* (Cu_2P_2).

Preparation.—By boiling phosphorus in a cupric sulphate solution.

Properties.—A black substance, decomposed by heat ($3Cu_2P_2 = Cu_6P_2 + 2P_2$). Phosphoretted hydrogen is evolved when it is added to a solution of potassic cyanide.

Cupric Oxysalts.

(16.) Cupric Sulphate.—*Sulphate of copper; blue vitriol; blue stone; blue copperas* ($CuSO_4,5H_2O$).

Molecular weight, 159·4 + 90. *Specific gravity, crystals*, 2·25. *Anhydrous*, 3·63.

Preparation—(1.) By dissolving the metal or its oxide in sulphuric acid.

(2.) By oxidising the sulphide.

(3.) As a secondary product in the refining of silver (*vide* silver); a cupric sulphate being formed from the copper plates used to throw down the silver from its solution as a sulphate.

Properties.—It is found in the form of transparent, blue, doubly oblique crystals ($CuSO_4,5H_2O$). When these are heated to 212° F. (100° C.) they become $CuSO_4,H_2O$, and at 392° F. (200° C.) the salt changes to a white anhydrous powder ($CuSO_4$). (This last H_2O molecule is regarded as water of constitution, the rest as water of crystallisation.) The anhydrous white salt combines energetically with water, the blue salt being thereby formed and great heat evolved. At a high temperature it is converted into cupric oxide, oxygen and sulphurous anhydride being evolved.

The crystals are insoluble in alcohol, but soluble in water (1 in 4 at 60° F., 1 in 2 at 212° F.). The solution is acid.

Potassic hydrate, added to a solution of the salt, throws down a blue hydrated cupric oxide or "blue verditer" (CuH_2O_2). The powdered

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crystals rapidly absorb hydrochloric acid gas, with evolution of heat. The anhydrous salt rapidly absorbs ammonia gas, forming $CuSO_4,5H_3N$ (Rose). With the sulphates of ammonium and potassium, cupric sulphate forms double salts, isomorphous with the corresponding magnesium salts—

$$\left(Cu''\begin{matrix}K_2\\(NH_4)_2\end{matrix}\right\} (SO_4)_2,\ 6H_2O \Big).$$

Several basic cupric sulphates are known: of these may be mentioned a *tribasic sulphate*, $CuSO_4,2CuH_2O_2$, and *brochantite*, $CuSO_4,3CuH_2O_2$.

The *ammonio-sulphate of copper* ($CuSO_4,4NH_3,H_2O$) is formed when a solution of cupric sulphate containing an excess of ammonia is carefully evaporated to dryness.

(17.) Cupric Nitrate ($Cu2NO_3,6H_2O$).

Preparation.—By dissolving copper in nitric acid.

Properties.—A blue crystalline deliquescent salt, soluble in alcohol, decomposed by a *slight* heat into an insoluble basic nitrate ($Cu2NO_3$, $3CuH_2O_2$), and by an *intense* heat into the black oxide (CuO).

Cupric Arsenite or *Scheele's green* ($CuHAsO_3$) is a green powder, prepared by the action of an alkaline arsenite on a cupric salt. A mixture of cupric arsenite and acetate ($3CuAs_2O_4,Cu2C_2H_3O_2$) constitutes "Schweinfurt green."

Basic phosphates of copper are found native as tagilite and libethenite.

The *cupric carbonates* known, are *a hydrated oxycarbonate* or "chessylite" ($2CuCO_3,CuH_2O_2$; Sp. Gr. 3·8), and *a hydrated dibasic carbonate* or "malachite" ($CuCO_3,CuH_2O_2$; Sp. Gr. 3·7). "Mineral green" has the same composition as this latter compound, and is prepared by acting on a solution of cupric sulphate with sodic carbonate. If the precipitate be boiled in the solution, CuO is formed.

Reactions of Copper.—(*See* ANALYTICAL TABLE.)

BISMUTH (Bi''').

Atomic weight, 210. *Specific gravity*, 9·83. *Fuses at* 507·2° F. (264° C.). *Atomicity, Triad* (*as in bismuthous compounds*) ($Bi'''Cl_3$); *and Pentad* (*as in bismuthic compounds* ($Bi^v{}_2O_5$).

Natural History.—Bismuth is commonly found in a free state, but it also occurs as an *oxide* (Bi_2O_3) as "bismuth ochre," and as a *sulphide* (Bi_2S_3) as "bismuth glance." These two last minerals are rare.

Preparation.—By simple fusion of the ore in inclined iron cylinders. Thus prepared, bismuth usually contains certain impurities, such as arsenic, sulphur, and silver, the latter being frequently extracted by cupellation.

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Properties.—(*α.*) *Physical.* A hard, brittle, reddish-white metal, crystallizing in large cubes. It is slightly volatile at high temperatures. It fuses at 507° F. (264° C.), expanding at the moment of solidification. Its admixture with other metals frequently lowers their fusing point to a remarkable extent.

(*β.*) *Chemical.* Bismuth is only slightly affected by air at ordinary temperatures, but it oxidizes rapidly when made red-hot. Nitric acid dissolves it freely; boiling sulphuric acid oxidizes it, SO_2 being evolved; hydrochloric acid and dilute sulphuric acid have no action upon it. It combines rapidly with chlorine, bromine, iodine, and sulphur.

No compound of bismuth with hydrogen is known.

Uses.—For alloys. Its use in type metal depends on its property of expanding as it solidifies, thereby increasing the sharpness of the impression.

In solder, its use depends on its power of lowering the fusing point of the alloy.

Compounds of Bismuth.

	SALTS.	Formula (General.)	Formula (Constitution.)	Molecular Weight.	Specific Gravity.	Bi. per cent.
1. Oxides.	Dibismuthous dioxide	Bi_2O_2	$\left\{\begin{matrix}BiO\\BiO\end{matrix}\right.$	448·0		92·85
2. Oxides.	Bismuthous oxide	Bi_2O_3	Bi_2O_3	468·0	8·211	89·74
3. Oxides.	Dibismuthic tetroxide	Bi_2O_3,Bi_2O_5 or Bi_2O_4	$Bi^{iv}{}_2O_4$	480·0		86·66
4. Oxides.	Bismuthic oxide or anhydride	Bi_2O_5		496·0		83·87
5. Chlorides.	Bismuthous chloride (trichloride) ..	$BiCl_3$	$BiCl_3$	314·5	4·56	66·13
6. Chlorides.	Bismuthous oxychloride	BiClO	BiOCl	259·5		80·15
7. Chlorides.	Dibismuthous tetrachloride (dichloride)	Bi_2Cl_4	$\left\{\begin{matrix}BiCl_2\\BiCl_2\end{matrix}\right.$	558·0		74·55
8.	Bismuthous bromide	$BiBr_3$	$BiBr_3$	448·0		46·42
9.	,, oxybromide		BiOBr	304·0		68·42
10.	Bismuthous iodide	BiI_3	BiI_3	589·0		35·31
11.	,, oxyiodide	BiIO	BiOI	351·0		59·25
12.	,, fluoride	BiF_3	BiF_3	265·0		78·49
13. Sulphides.	Dibismuthous disulphide	Bi_2S_2	$'B''_2S''_2$	480·0		86·66
14. Sulphides.	Bismuthous sulphide	Bi_2S_3	$Bi_2S'_3$	512·0		81·25
15.	,, nitrate	$Bi3NO_3,5H_2O$	$\left\{\begin{matrix}NO_3\\NO_2Bio''',5H_2O\\NO_2\end{matrix}\right.$	394·0	2·376	52·79

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COMPOUNDS OF BISMUTH WITH OXYGEN AND HYDROXYL.

Dibismuthous dioxide ... ... Bi_2O_2; $\left\{\begin{matrix}\mathbf{BiO}\\\mathbf{BiO}\end{matrix}\right.$

Bismuthous oxide ... ... Bi_2O_3; $\mathbf{Bi_2O_3}$

[Metabismuthous acid $(Bi_2O_3,H_2O)=HBiO_2$ or **Bi**OHo]

Bismuthic oxide or anhydride... ... Bi_2O_5; $\mathbf{Bi_2O_5}$

[Metabismuthic acid $(Bi_2O_5,H_2O)=HBiO_3$ or $\mathbf{BiO_2Ho}$]

Dibismuthic tetroxide or Bismuthous bismuthate } (Bi_2O_3,Bi_2O_5) or Bi_2O_4; $'\mathbf{Bi^{iv}}_2O_4$.

(1.) Dibismuthous Dioxide (Bi_2O_2). *Preparation.* By reducing bismuthous chloride with stannous chloride in the presence of an excess of potash.

Properties.—It burns freely, forming Bi_2O_3.

(2.) Bismuthous Oxide; *Sesquioxide* or *Trioxide of Bismuth* (Bi_2O_3). *Molecular weight*, 468. *Specific gravity*, 8·2.

It is found native as "bismuth-ochre."

Preparation.—(1.) By heating bismuth in air. (2.) By igniting the nitrate or carbonate.

Properties.—A yellow, easily fusible powder, soluble in HCl, in HNO_3, and in H_2SO_4, forming *bismuthous chloride* ($BiCl_3$), *bismuthous nitrate* (Bi 3(NO_3)), and *bismuthous sulphate* (Bi_2 3(SO_4)) respectively. Ammonia precipitates the oxide as a hydrate from the solution of a salt of bismuth (Bi_2O_3,H_2O).

(3.) Metabismuthous Acid ($Bi_2O_3,H_2O=HBiO_2=$**Bi**OHo).

Preparation.—By adding ammonia to a solution of bismuthous nitrate in dilute nitric acid. When heated, a residue of Bi_2O_3 remains. By the fusion of Bi_2O_3 with sodic carbonate, a *sodic metabismuthite* ($NaBiO_2$) is formed.

(4.) Bismuthic Oxide; *Pentoxide* or *Anhydride* (Bi_2O_5).

Preparation.—(*a.*) When bismuthous oxide, suspended in a solution of potassic hydrate, is treated with chlorine, *metabismuthic acid* ($HBiO_3$) is formed.

$4KHO$	$+$	$2Cl_2$	$+$	Bi_2O_3	$=$	$2HBiO_3$	$+$	$4KCl$	$+$	H_2O.
Potassic hydrate	+	Chlorine	+	Bismuthous oxide	=	Metabismuthic acid	+	Potassic chloride	+	Water.

(*β.*) By heating the $2HBiO_3$ ($=Bi_2O_5,H_2O$) to 269° F. (132° C.), the H_2O is expelled and *bismuthic oxide* remains.

Properties.—A red powder, decomposed by heat ($2Bi_2O_5=Bi_2O_3,Bi_2O_5$ (or $2Bi_2O_4$)$+O_2$) into *bismuthous bismuthate.* When bismuthic oxide is heated in a current of hydrogen, Bi_2O_3 is formed. Heated with hydrochloric acid it forms bismuthous chloride, chlorine being evolved ($Bi_2O_5+10HCl=2BiCl_3+5H_2O+2Cl_2$). When treated with nitric or with sulphuric acids a bismuthous nitrate or sulphate is formed accordingly, oxygen being liberated ($Bi_2O_5+6HNO_3=2Bi3NO_3+3H_2O+O_2$).

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Metabismuthic Acid ($Bi_2O_5,H_2O=HBiO_3$ or BiO_2Ho).

Preparation.—*Vide* (*a*), under bismuthic oxide. The compounds of this acid are very unstable.

COMPOUNDS OF BISMUTH AND CHLORINE.

Bismuthous chloride	... ...	$BiCl_3$.
Dibismuthous tetrachloride	... ...	Bi_2Cl_4.

(5.) Bismuthous Chloride.—*Trichloride of bismuth* ($BiCl_3=316{\cdot}5$).

Molecular weight, 316·5. *Specific gravity of solid*, 4·56 ; *of vapor*, 11·16. *Molecular volume*, |_|_|.

Preparation.—(1.) By heating bismuth in a current of chlorine ($Bi_2+3Cl_2=2BiCl_3$).

(2.) By distilling a mixture of bismuth and mercuric chloride ($Bi_2+6HgCl_2=2BiCl_3+3'Hg'_2Cl_2$).

(3.) By distilling a solution of bismuth in nitro-hydrochloric acid.

Properties.—A fusible, volatile, deliquescent solid. It is soluble in dilute hydrochloric acid, but is decomposed by pure water into bismuthous oxychloride [$3BiClO = (BiCl_3,Bi_2O_3)$], or "pearl white," and hydrochloric acid ($BiCl_3+H_2O=BiClO+2HCl$). The oxychloride is insoluble in tartaric acid, or in ammonic sulphide.

COMPOUNDS OF BISMUTH AND SULPHUR.

Dibismuthous disulphide	...	Bi_2S_2	... $''\mathbf{Bi}''_2S''_2$.
Bismuthous sulphide	...	Bi_2S_3	... $\mathbf{Bi}_2S'_3$.

Dibismuthous Disulphide (Bi_2S_2) is found native, and may be prepared by fusing together sulphur and bismuth.

(13, 14.) Bismuthous Sulphide ($Bi_2S_3=516$) is found native as "bismuth glance."

Preparation.—(1.) By fusing together sulphur and bismuth in proper proportions.

(2.) By passing sulphuretted hydrogen through a bismuth solution ($2BiCl_3+3H_2S=Bi_2S_3+6HCl$).

Properties.—A fusible, dark grey, heavy substance (Sp. Gr. 6·4). It is soluble in nitric acid, but is insoluble in either dilute sulphuric, or hydrochloric acids, or in the alkaline hydrates or sulph-hydrates.

OXYSALTS OF BISMUTH.

(15.) Bismuthous Nitrate ($Bi3NO_3$, $5H_2O=396+90$, Sp. Gr. 2·3).

Preparation.—By dissolving the metal in nitric acid.

Properties.—When the acid solution is acted on with a quantity of water, a precipitate is thrown down of a *basic nitrate, subnitrate,* or *trisnitrate of bismuth* (flake white; magistery of bismuth) ($Bi3NO_3$, $Bi_2O_3,3H_2O$).

Reactions of Bismuth.—(*See* ANALYTICAL TABLES.)

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CADMIUM (Cd″).

Atomic and molecular weight, 112. *Specific gravity*, 8·604. *Fuses at* 442° F. (228° C.), *Boils at* 1580° F. (860° C). *Atomicity*, *dyad* ($CdCl_2$; CdO).

History.—Discovered by Stromeyer (1818).

Natural History.—Cadmium is found in zinc ores, and also as a sulphide (Greenockite).

Preparation.—When zinc ore is distilled, the cadmium (a constant accompaniment of zinc) passes over first, owing to its greater volatility, its presence being indicated by a *brown* flame (brown blaze). The distillate thus obtained (a mixture of cadmium and zinc) is dissolved in dilute sulphuric acid, and H_2S passed through the solution. The yellow precipitate of CdS formed, is then dissolved in hydrochloric acid, to which an excess of ammonic carbonate is added. The precipitated carbonate of cadmium ($CdCO_3$), on ignition becomes CdO, from which the metal may be obtained by distillation with charcoal.

Properties.—(*α.*) *Physical.* A white, soft, crystalline metal, marking paper like lead, and crackling when bent like tin. At common temperatures it is both malleable and ductile, but when heated to 176° F. (80° C.) it becomes brittle. It fuses at 442° F. (228° C.) The cadmium atom appears to occupy in the state of vapor twice the space of the hydrogen atom.

(*β.*) *Chemical.*—At ordinary temperatures air has no action upon the metal, but it burns with a brown flame when heated, CdO being formed. The metal is dissolved by the mineral acids when heated with them, hydrogen being evolved.

Uses.—Its presence in alloys reduces the fusing point of the alloy, without impairing the toughness or the malleability of the compound.

COMPOUNDS OF CADMIUM WITH OXYGEN, WITH THE HALOIDS, AND WITH SULPHUR.

Cadmic oxide	...	...	CdO
Cadmic chloride	...	...	$CdCl_2$.
Cadmic sulphide	...	...	CdS.

Cadmic Oxide (CdO=128) is a brown powder, prepared either by burning the metal in air, or by igniting the nitrate. A *cadmic hydrate* (CdH_2O_2) is formed by precipitating a cadmic salt with potassic hydrate.

Cadmic Chloride ($CdCl_2,2H_2O$), **Cadmic Iodide** (a salt used in photography), and **Cadmic Sulphide** (CdS=144) (Greenockite), a bright yellow pigment of great purity and permanence, have been prepared. The yellow cadmic sulphide may be known from the yellow orpiment by being non-volatile, and insoluble in ammonic sulphide.

Reactions of Cadmium.—(*See* ANALYTICAL TABLE.)

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PALLADIUM (Pd″=106·5).

Atomic weight, 106·5. *Specific gravity*, 11·6. *Fusing point*, 2480° F., (1360° C.). *Atomicity, dyad* (″) *as in palladious compounds*, (*e.g.*, $PdCl_2$); *rarely tetrad* (^{iv}) *as in palladic compounds* ($PdCl_4$).

History.—Discovered by Wollaston (1803) in platinum ores (0·5 to 1 per cent.).

Natural History.—Found associated with platinum and gold.

Extraction.—(α.) *Extraction from platinum ores.* After the platinum has been precipitated from its solution by ammonic chloride, the filtrate is neutralised and the palladium precipitated as palladic cyanide with mercuric cyanide. This precipitate of palladic cyanide is collected and heated to redness, the spongy palladium thus obtained being afterwards heated, hammered, and welded.

(β.) *Extraction from gold ores.*—The gold ore is first fused with silver. The fused mass is then boiled with nitric acid, whereby the gold is separated as an insoluble precipitate. The silver in the solution is then precipitated with sodic chloride. The lead, copper, and palladium are afterwards separated from the filtrate by placing a piece of metallic zinc in the liquid. The mixed precipitate thus obtained is then dissolved in nitric acid, from which the lead is precipitated by ammonia, leaving the copper and the palladium only in solution. The palladium is then precipitated as *hydrochlorate of palladamine* ($Pd''N_2H_4,2HCl$) by the addition of hydrochloric acid in excess. This precipitate, when heated, leaves the pure metal .

Properties.—(α.) *Physical.* A hard, white metal, malleable and ductile, harder and lighter than platinum (Sp. Gr. 11·6). It is volatile at a high temperature, when it evolves green vapors. At a red heat the metal absorbs oxygen, but liberates it again on cooling. It possesses the property of absorbing many times its volume of hydrogen, giving it out again at high temperatures. This property is far more marked in the *hammered* palladium, which will absorb 640 times its volume of hydrogen, than with the *fused* metal, which only absorbs 68 times its bulk.—("Proceedings Royal Society," June, 1866.)

(β.) *Chemical.* Palladium is unaffected by air at ordinary temperatures. At a low red heat it becomes oxidized; but at a higher temperature the oxide formed at the lower temperature is reduced. It is soluble in nitric acid, forming palladious nitrate ($Pd(NO_3)_2$), and also in aqua regia. It is oxidized by fusion with the caustic alkalies, nitre, etc. It combines with iodine, forming palladious iodide (PdI_2). Hence, if an alcoholic solution of iodine be evaporated on palladium, a stain of PdI_2 is produced, a reaction which serves to distinguish palladium from platinum. It forms a carbide when heated in the flame of a spirit lamp. With gold (1Pd and 4Au) it forms a perfectly white brittle alloy; with silver (1Pd and 2Ag) it forms a white unoxidizable alloy of

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great ductility, and useful for small weights; and with tin (1Pd and 8Sn=Pd_3Sn_2) it forms an alloy of great brilliancy.

Compounds of Palladium.

	SALTS.	Formula (General).	Formula (Constitutional).	Molecular Weight.	Pd per cent.
1.	Oxides. Suboxide of palladium	Pd_2O	$'Pd'_2O$	229·0	93·01
2.	Oxides. Palladious oxide	PdO	$Pd''O$	122·5	86·93
3.	Oxides. Palladic oxide	PdO_2	$Pd^{iv}O_2$	138·5	76·89
4.	Chlorides. Palladious chloride	$PdCl_2$	$Pd''Cl_2$	177·5	60·00
5.	Chlorides. Palladic chloride	$PdCl_4$	$Pd^{iv}Cl_4$	248·5	42·89
6.	Palladious iodide	PdI_2	$Pd''I_2$	360·5	Pd 29·54 I 70·46
7.	Palladious cyanide	$PdCy_2$	$Pd''Cy_2$	158·5	
8.	Sulphides. Subsulphide of palladium	Pd_2S	$'Pd'_2S$	245·0	
9.	Sulphides. Palladious sulphide	PdS	$Pd''S$	138·5	
10.	Sulphides. Palladic sulphide	PdS_2	$Pd^{iv}S_2$	170·5	62·46

(1.) The Suboxide of Palladium (Pd_2O) is prepared by heating hydrated palladious oxide (PdH_2O_2) to redness.

(2.) Palladious Oxide (PdO) is prepared as a *brown hydrate* (PdH_2O_2) soluble in acids and in alkalies, by adding potassic carbonate to a palladious salt, or in an *anhydrous* form, either by heating the hydrate, or by the ignition of the nitrate.

(3.) Palladic Oxide (PdO_2) is prepared as a yellowish-brown hydrate($Pd^{iv}H_4O_4$) by acting on potassic palladic-chloride($2KCl,PdCl_4$) with a solution of potassic hydrate. It may be obtained in an anhydrous form as a black powder by boiling the hydrate in water.

(4.) Palladious Chloride; *Chloride of Palladium.* ($Pd''Cl_2$=177·5).

Preparation.—By evaporating a solution of the metal to dryness.

Properties.—The hydrate is brown, and the anhydrous compound black. It is decomposed by heat, the metal being reduced. It forms double salts of a dark green color with the alkaline and with other metallic chlorides. With ammonia it forms a series of compounds similar to those formed by platinum, palladamine being isomeric with platinamine, etc. (*See* page 406.)

(5.) Palladic Chloride ($Pd^{iv}Cl_4$) is only known in solution. It forms double salts with the alkaline chlorides, as *e.g.*, the red, and somewhat insoluble salt ($2KCl,PdCl_4$.) It is easily decomposed into palladious chloride and free chlorine.

(6.) Palladious Iodide ($Pd''I_2$).

Preparation.—By the action of a soluble iodide on a soluble palladious salt.

Properties.—A black substance, insoluble either in water, ammonia,

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or in an excess of potassic iodide. It is decomposed by a heat of 662° F. (350° C.).

[N.B.—In the laboratory, palladium salts are used for the estimation of iodine, as they do not precipitate either chlorine or bromine.]

(7.) Palladious Cyanide ($Pd''Cy_2$).

Preparation.—By acting on neutral solutions of palladious salts with potassic or mercuric cyanide.

Properties.—A yellow substance, soluble in ammonia, in acids, and in an excess of potassic cyanide.

(9.) Palladious Sulphide ($Pd''S$) is formed by precipitating a palladious salt with sulphuretted hydrogen. It is insoluble in ammonic sulphide.

Reactions of Palladium Compounds.

1. *Sulphuretted hydrogen;* a black ppt. ($Pd''S$), insoluble in ammonic sulphide.
2. *Mercuric cyanide;* a yellow ppt. ($Pd''Cy_2$) in neutral solutions.
3. *Potassic iodide;* a black ppt. ($Pd''I_2$), soluble in excess.
4. *Potassic and sodic hydrates;* a red or brown ppt., soluble in excess.
5. *Potassic and sodic carbonates;* a brown precipitate of $Pd''H_2O_2$, with salts of Pd''.
6. *Ammonia and ammonic carbonates;* a flesh-colored ppt. with $Pd''Cl_2$, soluble in excess of ammonia.

Estimation of palladium as palladious iodide:—100 grs. = 29·54 Pd.

RHODIUM (Rh = 104·3).

Specific gravity, 12·1. *From its analogy, regarded as a tetrad* (^{iv}) (Rh_2Cl_6).

History.—Discovered by Wollaston (1803).

Natural History.—Found in platinum ores (0·5 per cent.).

Extraction.—It is obtained from the solution of the platinum ore. The filtrate, after the extraction of the platinum (by NH_4Cl) and of the palladium (by mercuric cyanide), is acidulated with hydrochloric acid. Sodic chloride is then added, and the liquid evaporated to dryness. On treating the residue with alcohol (Sp. Gr. 0·837) everything is dissolved, except the double chloride of rhodium and sodium—

$$(Rh_2Cl_6, 6NaCl, 24H_2O),$$

which remains as a red powder. From this compound, metallic rhodium may be obtained, either by placing bars of zinc in a solution of the compound, or by heating the dry salt itself in a current of hydrogen, the sodic chloride being afterwards removed by washing.

Properties.—(α.) *Physical.* A white hard brittle metal (Sp. Gr. 12·1). It requires a greater heat for its fusion, than even platinum. It absorbs oxygen when melted.

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(β.) *Chemical.*—It is oxidised when heated in air. It is insoluble in acids if pure, but is soluble in nitro-hydrochloric acid, when alloyed with platinum, lead, etc., provided these latter metals be present in excess. It combines with sulphur by heat (RhS). It is dissolved when fused with potassic nitrate. By fusion with hydric potassic sulphate, a soluble potassic rhodic sulphate ($KRh2SO_4$) is formed.

Compounds of Rhodium.

		SALTS.	Formula (General).
1.	Oxides.	Protoxide of rhodium	RhO
2.		Rhodic oxide	Rh_2O_3
		„ „ hydrates of	RhH_3O_3 / RhH_3O_3,H_2O
3.		Dioxide of rhodium	RhO_2
4.		Trioxide of rhodium	RhO_3
5.	Chlorides.	Rhodic chloride	Rh_2Cl_6
6.		Sodic rhodic chloride	$6NaCl,Rh_2Cl_6,24H_2O$
7.		Potassic rhodic chloride	$6KCl,Rh_2Cl_6,6H_2O$
8.		Ammonic rhodic chloride	$6NH_4Cl,Rh_2Cl_6,3H_2O$
9.	Sulphides.	Protosulphide of rhodium	RhS
10.		Sesquisulphide of rhodium	Rh_2S_8
11.		Rhodic sulphate	$Rh_2(SO_4)_3 12H_2O$
12.		Potassic rhodic sulphate	$RhK_3(SO_4)_3$

Reactions of the Rhodium Compounds.

1. *Sulphuretted hydrogen;* a brown ppt. (Rh_2S_3) in a hot solution, insoluble in ammonic sulphide.

2. *Soluble sulphites;* a pale yellow ppt.

3. *Potassic iodide;* a yellow ppt. (Rh_2I_6).

4. *Fixed alkalies;* a yellow ppt. ($Rh_2O_3,5H_2O$), soluble in acids and in excess of alkali.

5. Solutions of rhodic salts (which are usually rose-colored) are decomposed, with precipitation of metallic rhodium, by iron or zinc.

6. The metal is reduced when heated in a current of hydrogen.

OSMIUM (Os).

Atomic weight, 199. *Specific gravity*, 21·4. *Atomicity dyad, tetrad and hexad.*

History.—Discovered by Tennant, 1803 (*Derivation*, ὀσμή, odor).

Natural History.—Is found in platinum ores.

Extraction.—The solution of the ore in potassic hydrate (*see preparation of Ruthenium*) is mixed with an excess of hydrochloric acid and metallic mercury, and digested in a closed bottle at 284° F. (140° C.). The mercury reduces the osmium, which immediately forms an amalgam with the excess of mercury, from which the mercury may be afterwards distilled, and the metallic rhodium obtained as a black powder—$OsO_4+8Hg+8HCl=Os+4Hg_2Cl_2+4H_2O$.

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Properties.—These vary. In the *state of powder* rhodium is black, and has a specific gravity of 10. It is highly combustible, and is easily oxidised by nitric or by nitro-hydrochloric acids to OsO_4. In the *compact state* (*i. e.*, after ignition) it exhibits great lustre. It has a specific gravity of 21·4, and is not soluble in acids. It is the least fusible of all the metals. A heat which fuses platinum, iridium and ruthenium, will not melt, although it may volatilise, osmium.

Compounds of Osmium.

	SALTS.	Formula (General.)	Molecular Weight.
1.	Protoxide of osmium	OsO	215
2.	Sesquioxide of osmium; osmious oxide	Os_2O_3	446
3.	Dioxide of osmium; osmic oxide	OsO_2	231
4.	Trioxide of osmium	OsO_3	247
5.	Tetroxide of osmium; osmic acid	OsO_4	263
6.	Protochloride of osmium; osmious dichloride	$OsCl_2$	270
7.	Trichloride of osmium	Os_2Cl_6	611
8.	Osmic chloride	$OsCl_4$	341
9.	Osmic hexachloride	$OsCl_6$	412
10.	Sulphide of osmium	OsS_4	327

(5.) **Osmic Tetroxide.**—(*Osmic acid*) (OsO_4) is formed when metallic osmium or the lower oxide of osmium is heated in air, or treated with aqua regia. It consists of colorless crystals, which are very volatile and intensely pungent. It is very soluble in water, the solution staining the skin black, and possesses a strong smell. It is a powerful oxidising agent. It is soluble in alkalies, forming yellow solutions. Sulphuretted hydrogen precipitates a black sulphide (OsS_4) from the alkaline solutions.

Reactions of Osmium Compounds.

1. They all yield a peculiar odor when heated with nitric acid.

2. *Sulphuretted hydrogen*, when passed through a solution of OsO_4, acidulated with HCl, gives a black ppt. (OsS_4), which is very slightly soluble in ammonic sulphide.

With Osmic Acid :—

1. *Potassic nitrite;* produces a red salt, potassic osmite.

2. *Sodic sulphite;* produces a blue salt, osmium sulphite.

RUTHENIUM (Ru).

Atomic weight, 104·4. *Specific gravity of porous metal*, 8·6, *and of fused metal*, 11·4.

Like the other platinum metals it is both a dyad ($RuCl_2$) *and a tetrad* ($RuCl_4$).

History.—Discovered by Claus (1846).

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Natural History.—Found in platinum ores: also in the mineral "laurite," as a sulphide, together with sulphide of osmium (Borneo).

Extraction.—When platinum ore is acted upon with aqua regia, an insoluble white scaly residue remains, consisting of an alloy of osmium, iridium, ruthenium, with a little rhodium. When this is heated in a current of air, the osmium is oxidised (OsO_4) and volatilises, the vapor being condensed either in flasks or in a solution of caustic potash. The osmic acid vapor, moreover, carries the ruthenium, as ruthenic oxide, mechanically with it, RuO_2 not being itself volatile. This is deposited on fragments of porcelain placed in immediate contact with the heated tube. The metallic ruthenium is prepared from this oxide by heating in hydrogen. Ruthenium and iridium are also found in the residue remaining in the tube. By fusing this residue with potassic hydrate, a potassic rutheniate is produced, which is soluble in water, from which solution Ru_2O_3 may be precipitated by nitric acid, and the oxide reduced by ignition in hydrogen.

Properties.—(*a.*) *Physical.* A hard, brittle, and almost infusible metal.

(*β.*) *Chemical.* It oxidises with difficulty when heated in air, but readily when heated with potassic hydrate or with potassic nitrate, potassic rutheniate being formed. This salt, dissolved in water, yields a yellow-colored solution.

Compounds of Ruthenium.

	SALTS.	Formula (General.)	Molecular Weight.
1.	Monoxide of ruthenium (dark grey)	RuO	120·4
2.	Sesquioxide of ruthenium; ruthenious oxide (black)	Ru_2O_3	256·8
3.	Ruthenic oxide	RuO_2	136·4
4.	,, anhydride (ruthenic acid)	RuO_3	152·4
5.	,, tetroxide	RuO_4	168·4
6.	Dichloride of ruthenium	$RuCl_2$	175·4
7.	Ruthenious chloride	Ru_2Cl_6	421·8
8.	Ruthenic chloride	$RuCl_4$	246·4
9.	Sesquisulphide of ruthenium	Ru_2S_3	304·8
10.	Ruthenic sulphide	RuS_2	168·4

(Oxides. 2–5; Chlorides. 6–8; Sulphides. 9–10)

Oxides of Ruthenium.—*The monoxide* (RuO) is a dark grey powder, not affected by acids. *Ruthenious oxide* (Ru_2O_3) and *ruthenic oxide* (RuO_2) are feeble bases. *Ruthenic anhydride* (RuO_3) is only known in combination. It is analogous to osmic anhydride.

Reactions of Ruthenium Compounds.

Dissolve the residue formed by fusing together caustic potash and a ruthenium compound, in water. Test the solution as follows:—

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1. *Nitric acid;* a black ppt. (Ru_2O_3).

2. Add *hydrochloric acid* to the liquid having the Ru_2O_3 (formed by test No. 1) in suspension. On applying heat, an orange yellow solution results.

3. Treat this solution with *sulphuretted hydrogen;* a black ppt. occurs, the filtrate appearing of a blue color.

4. *Plumbic acetate;* a purple red ppt.

B.—Metals whose Sulphides are Soluble in the Alkaline Sulphides.

TIN (Sn).

Atomic weight, 118. *Specific gravity,* 7·28. *Fusing point,* 442·4° F. (228° C). *Atomicity, dyad as in stannous salts* (*as* $Sn''O$; $Sn''Cl_2$); *and tetrad, as in stannic salts* ($Sn^{iv}O_2$; $Sn^{iv}Cl_4$).

History.—The metal was known to the ancients.

Natural History.—Found in veins as "tin stone" (SnO_2) in the granite and quartz (mine-tin). Also found in small round masses in alluvial soils (stream-tin ore). It is often found associated both with arsenical iron pyrites, and also with manganese and iron oxides, and with tungstic anhydride (WO_3), in the mineral called "wolfram."

Preparation.—(*a.*) The ore is first crushed, and afterwards washed, to remove foreign matters (Sp. Gr. of quartz 2·7; of SnO_2 6·5).

(*β.*) The washed ore is then *roasted,* by which means the arsenic (as As_2O_3) and the sulphur (as SO_2) are expelled. The iron present after roasting exists as Fe_2O_3, and the copper chiefly as sulphate. To effect the complete conversion of the sulphide into sulphate of copper, the roasted ore, damped with water, is exposed to the air for some days.

(*γ.*) The mass is now treated with water, which dissolves out the cupric sulphate, and mechanically washes away much of the ferric oxide, owing to the specific gravity of the ferric oxide being very much less than that of the stannic oxide.

(*δ.*) The residual tin ore is now *reduced.* This is effected by mixing it with powdered coal and a little lime, and subjecting the mixture to heat in a reverberatory (reducing) furnace. The *coal* reduces the SnO_2, CO being evolved, whilst the *lime* forms a fusible slag with the earthy impurities.

(*ε.*) The reduced metal is then *refined.* Crude tin contains iron, arsenic, copper and tungsten. The purest portions of metal, being less fusible than the alloy, melt first, thus permitting their easy separation. The purity of the tin is roughly shown by its breaking up into irregular prismatic fragments (dropped or grain tin), when the hot ingots are struck with a hammer.

Properties.—(*a.*) *Physical.* A white metal, soft and malleable, but not ductile, unless heated to 212° F. (100° C.). It is very wanting

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both in tenacity and elasticity. It crackles when bent, developing heat. Its smell when rubbed is peculiar. It may be made to crystallise by slow cooling. Its crystalline character is well shown in the *moirée métallique*, which is prepared by washing tin plate with dilute nitro-hydrochloric acid. It fuses at 442° F. (227° C.), but is not volatile. It is a good conductor of heat and electricity.

(*β.*) *Chemical.* At ordinary temperatures tin is unacted upon either by air or by water, singly or conjointly. It burns in air at a high temperature, with a white light, forming "putty powder" (SnO_2). When red-hot it decomposes steam, an oxide of the metal being formed.

Action of acids.—Strong nitric acid (Sp. Gr. 1·5)has no action upon it; dilute nitric acid (Sp. Gr. 1·3) does not dissolve it, but forms with it the insoluble metastannic acid ($H_2Sn_5O_{11},4H_2O$), and ammonia, this latter resulting from the decomposition of the water. When strong sulphuric acid is boiled with it, it converts it into stannic sulphate ($Sn2SO_4$), SO_2 being evolved with the separation of sulphur, the latter probably resulting from the stannous sulphate becoming oxidised to stannic sulphate, at the expense of the oxygen of the sulphurous anhydride. Dilute sulphuric acid has no action upon it. Strong hydrochloric acid dissolves it when heated, hydrogen being evolved. It is soluble in aqua regia, $SnCl_4$ being formed.

The fixed alkaline hydrates, when heated with the metal, dissolve it, hydrogen being evolved, and an alkaline metastannate formed. Tin combines readily by heat with sulphur, with phosphorus, and with the haloids.

Impurities.—Lead, iron, copper, arsenic, antimony, bismuth, gold and tungsten.

Uses.—*Tin-foil. Tin plate* (which consists of iron coated with tin). The iron, after being freed from adhering oxide by immersion in acids, and by subsequent scouring and washing, is dipped into melted tin. Sometimes the dipped plate is hammered, in order to effect the more perfect union of the tin and iron (block tin). If the covering of the tin be imperfect, the corrosion of the iron is rendered more rapid, a galvanic couple being formed, which decomposes the water, the oxygen of which rusts the iron. In *tinning copper vessels*, any oxide on the copper is first removed by rubbing it over with ammonic chloride, and heating ($CuO+2NH_4Cl=CuCl_2+H_2O+2NH_3$).

Pins are made from brass wire tinned by boiling in water containing cream of tartar, alum, sodic chloride and granulated tin. An acid solution of tin is formed, from which the tin is thrown down on the brass by electrolysis.

Tin forms an important ingredient of many alloys, as *e. g.*, *Britannia metal* (Brass, Sn,Sb,Bi); *pewter* (Sn,Pb); *speculum metal* (Cu,Sn, a little As); *bell metal, gun metal and bronze* (Cu,Sn); *bronze coin* (Cu,Sn,Zn); *type metal* (Sn,Sb,Pb); *solder*, such as *fine solder* (2Sn1Pb), *common*

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solder (1Sn and 1Pb), *coarse solder* (1Sn and 2Pb). An amalgam of tin and mercury is used for silvering mirrors.

Compounds of Tin.

	SALTS.	Formula (General).	Formula (Constitutional).	Molecular Weight.	Specific Gravity.	Sn per cent.
1.	Oxides. Stannous oxide (protoxide of tin)	$Sn''O$	SnO	134		88·06
2.	Sesquioxide of tin ..	Sn_2O_3	$\left\{\begin{matrix}SnO\\SnO_2\end{matrix}\right.$			
3.	Stannic oxide (binoxide of tin)	SnO_2	SnO_2	150	6·95	78·66
4.	Metastannic acid	$Sn_5O_{10},5H_2O$	$Sn_5O_5H_{10}$	840		70·23
5.	Stannic acid	H_2SnO_3	$SnOH_2$	168		
6.	Chlorides. Stannous chloride (protochloride)	$Sn''Cl_2$	$SnCl_2$	189		62·43
7.	Stannic chloride (bichloride, tetrachloride) .. (Bromides and iodides similar to chlorides.)	$Sn^{IV}Cl_4$	$SnCl_4$	260	2·234	45·38
8.	Sulphides. Stannous sulphide (protosulphide)	SnS	SnS″	150		78·66
9.	Distannic trisulphide (sesquisulphide of tin)	Sn_2S_3	$\left\{\begin{matrix}SnS''\\SnS''S''\end{matrix}\right.$			
10.	Stannic sulphide (disulphide)	SnS_2	SnS''_2	182		
11.	Stannic sulphate	$Sn2SO_4$				

Compounds of Tin and Oxygen.

Stannous oxide	SnO.
Sesquioxide of tin	Sn_2O_3.
Stannic oxide	SnO_2.
Metastannic acid	$5SnO_25H_2O$.
Stannic acid	SnO_2,H_2O.

(1.) Stannous Oxide.—*Protoxide of tin* (SnO).

Preparation.—(1.) (*As a hydrate* [$2SnO,H_2O$]). By adding an excess of an alkaline carbonate to a solution of stannous chloride.

(2.) (*Anhydrous*). By igniting the hydrate in nitrogen or in carbonic anhydride.

(3.) By heating stannous oxalate in closed vessels. (If heated in the open air it forms SnO_2.)

Properties.—The hydrate is a white body freely absorbing oxygen from the air. It is soluble when boiled in a strong solution of potassic hydrate, but if the boiling be long continued, or if the solution be kept for some time, the metal is precipitated and SnO_2 remains in solution. It is soluble in acids. With sulphuric acid it

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forms stannous sulphate ($Sn''SO_4$). The anhydrous oxide is a black permanent body, and burns like tinder, forming SnO_2.

(2.) **The Sesquioxide of Tin** (Sn_2O_3) is but little understood.

(3.) **Stannic Oxide.**—*Binoxide of tin* (SnO_2) is found native as tin-stone. It is formed whenever the metal or stannous oxide is heated in air. It is insoluble in acids, but forms soluble compounds when boiled with the alkalies. It forms two hydrates, both of which are acids, as follows:—

(4.) (*a.*) **Metastannic Acid** ($5SnO_2,10H_2O$) is formed by the action of nitric acid on tin. When this product is dried at 212° F. (100° C.) it becomes $5SnO_2,5H_2O$, a white powder insoluble either in water or in acids. By the further action of heat it changes to a yellow color (probably becoming anhydrous), forming what is called "putty powder," a substance used as a plate polisher. The acid forms non-crystallizable salts called "*metastannates*," in which one-fifth of the hydrogen of the acid is replaced by a metal—

$$\left[\begin{matrix}K_2O\\4H_2O\end{matrix}\right\} (SnO_2)_5\Big].$$

(5.) (*β.*) **Stannic Acid** (SnO_2,H_2O) is formed when an alkali is added to a solution of stannic chloride. It is soluble in acids, and also in cold solutions of potassic and sodic hydrates, forming crystallisable salts called "*stannates*," in which the whole of the hydrogen of the acid is exchanged for the metal (*e.g.*, SnO_2,Na_2O).

Sodic Stannate ($SnO_2,Na_2O,4H_2O$) forms the "Tin Prepare Liquor" of the calico-printer.

COMPOUNDS OF TIN AND CHLORINE.

Stannous chloride	...	...	...	$SnCl_2$.
Stannic chloride	...	...	...	$SnCl_4$.

(6.) **Stannous Chloride.**—*Protochloride of tin; Tin salt* ($SnCl_2$).

Preparation.—(1.) (*As a hydrate.*) By dissolving tin in hydrochloric acid, and evaporating down the solution until it crystallises ($SnCl_2,2H_2O$; Sp. Gr. 2·7).

(2.) (*Anhydrous.*) By heating the hydrate to 212° F. (100° C.).

Properties.—It has a strong attraction for chlorine, and also for oxygen, absorbing the latter from the air, whether exposed in a solid form or in solution, a mixture of stannic chloride and stannic oxychloride being formed. Hence the use of stannous chloride as a reducing agent;—dechlorinating chlorides;—deoxidising salts of mercury, silver and gold;—converting ferric and cupric salts into ferrous and cuprous salts;—depriving sulphurous acid of its oxygen, whereby a yellow precipitate of stannic sulphide is thrown down;—deoxidising indigo;—reducing combined metallic acids (such as CrO_3,As_2O_5, etc.) to a lower state of oxidation. When mixed with a quantity of water, stannous chloride is decomposed, a white hydrated oxychloride being formed

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($SnCl_2,SnO,2H_2O$). It is also decomposed by heat. It forms double crystallisable chlorides.

Stannous chloride constitutes the "tin crystals," or "salts of tin," of the dyer. It is commonly dissolved for use in a copper vessel, its solubility being increased by the resulting voltaic action.

(7.) Stannic Chloride.—*Bichloride and tetrachloride of tin; fuming liquor of Libavius* ($SnCl_4$).

Preparation.—(1.) (*As a hydrate.*) By heating tin with nitric and hydrochloric acids.

(2.) (*Anhydrous.*) By passing chlorine over metallic tin.

(3.) By distilling together powdered tin (1 part) and corrosive sublimate (5 parts) ($2HgCl_2+Sn=SnCl_4+Hg_2$).

Properties.—A thin colorless fuming liquid, boiling at 239·5° F. (115·3° C.); Sp. Gr. 2·234. It has a vapor density of 9·2. When mixed with a little water, it solidifies to a soft mass called "butter of tin" ($SnCl_4,5H_2O$). On adding an excess of water to stannic chloride, hydrated stannic acid is thrown down. It forms numerous double salts, as *e.g.*, the "pink salt" of the dyer ($2H_4NCl,SnCl_4$). It is largely used by dyers (nitro-muriate of tin) for the purpose of fixing and brightening red colors.

COMPOUNDS OF TIN AND SULPHUR.

Stannous sulphide	SnS.
Sesquisulphide of tin	Sn_2S_3.
Stannic sulphide	SnS_2.

(8.) Stannous Sulphide.—*Protosulphide of tin* (SnS). Found native as "tin pyrites."

Preparation.—(1.) By fusing together tin and sulphur.

(2.) By passing sulphuretted hydrogen through a solution of a stannous salt.

Properties.—A blackish grey body, soluble in hot hydrochloric acid, sulphuretted hydrogen being evolved.

(9.) Sesquisulphide of Tin (Sn_2S_3) is prepared by heating stannous sulphide with one-third its weight of sulphur.

(10.) Stannic Sulphide.—*Disulphide of tin; mosaic gold; bronze powder* (SnS_2).

Preparation.—(1.) By heating together, at a low red heat, tin (12 parts), mercury (6 parts), ammonic chloride (6 parts), and sulphur (7 parts).

(2.) By passing sulphuretted hydrogen through a solution of stannic chloride.

Properties.—A yellow-colored body, used in the arts as an imitation of gold or bronze. It is soluble in solutions of the alkaline hydrates

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when heated, and also in aqua regia, but is insoluble in nitric or in hydrochloric acids.

Tests for Tin.—(*See* ANALYTICAL TABLES.)

ANTIMONY (Sb).

Atomic weight, 122. *Molecular weight*, 488. *Specific gravity*, 5·7 to 6·7. *Fusing point*, 842° F. (450° C.). *Atomicity, a triad in antimonious salts* ($SbCl_3$; Sb_2O_3), *and a pentad in antimonic salts* ($SbCl_5$; Sb_2O_5).

History.—Discovered by Basil Valentine.

Natural History.—It is found native, but more commonly occurs as *stibnite*, or *grey antimony ore* (Sb_2S_3).

Preparation.—(1.) By melting out the antimony (owing to its ready fusibility) from the metals with which it is alloyed (*crude antimony*).

2. (α.) The ore (Sb_2S_3) is first *roasted*, in order to drive off some of the sulphur and arsenic present.

(β.) The roasted ore, which consists of a mixture of oxide (Sb_2O_3) and sulphide (Sb_2S_3), is now fused with charcoal and sodic carbonate (*regulus of antimony*). The sodic carbonate converts any sulphide present into oxide ($Sb_2S_3 + 3Na_2CO_3 = 3CO_2 + 3Na_2S + Sb_2O_3$), whilst the carbon reduces the oxide to the metallic state ($Sb_2O_3 + 3C = 3CO + Sb_2$).

(3.) An *amorphous* form of the metal may be prepared by the electrolysis of a solution of tartar emetic in antimonious chloride.

Properties.—(α.) *Physical.* A bluish-white, brittle metal, either crystalline or amorphous. It fuses at 842° F. (450° C.), and volatilises at a bright red heat. In solidifying it expands. Its power of conducting heat and electricity is comparatively small.

(β.) *Chemical.*—At ordinary temperatures antimony is unacted upon by the air, but when heated it burns, forming Sb_2O_3 (antimonious oxide). It fuses and fires when thrown into chlorine, and also combines with bromine and iodine when brought into contact with them, with the evolution of heat. Nitric acid oxidises it to antimonic anhydride (Sb_2O_5), which is insoluble in the acid. It readily dissolves by heat in aqua regia, and also in hydrochloric acid, hydrogen being evolved. It is soluble in potassic sulphide.

Uses.—It is used in the preparation of several alloys, such as *type metal* (2Pb, 1Sn, and 1Sb), a compound that expands slightly on cooling; *Britannia metal* (9Sn, 1Sb); *pewter* (12Sn, 1Sb, and Cu), etc. It is used in medicine.

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Compounds of Antimony.

	SALTS.	Formula (General.)	Formula (Constitutional.)	Molecular Weight.	Specific Gravity.	Sb per cent.
1.	Antimoniuretted hydrogen (stibine) ..	H_3Sb	SbH_3	125·0		97·60
2.	Oxides. Antimonious oxide (teroxide)	Sb_2O_3	Sb_2O_3	292·0		83·56
3.	Oxides. Antimonic oxide or anhydride (antimonic acid)	Sb_2O_5	Sb_2O_5	324·0		
4.	Oxides. Antimonious antimoniate	Sb_2O_3,Sb_2O_5	SbO_2SbO''	308·0		
5.	Chlorides. Antimonious chloride	$SbCl_3$	$SbCl_3$	228·5		53·39
6.	Chlorides. Antimonic chloride ..	$SbCl_5$	$SbCl_5$	299·5		
7.	Chlorides. Antimonious bromide	$SbBr_3$	$SbBr_3$			
8.	,, iodide..	SbI_3	SbI_3			
9.	,, fluoride(?)	SbF_3	SbF_3			
10.	Sulphides. Antimonious sulphide	Sb_2S_3	Sb_2S_3	340·0	4·6	71·77
11.	Sulphides. Antimonic sulphide ..	Sb_2S_5	Sb_2S_5	404·0		60·4

(1.) Antimoniuretted (or Antimonetted) Hydrogen; *Stibine; Antimonious hydride* (H_3Sb).

Preparation.—By acting either (α.) on zinc mixed with any antimonious salt, or (β.) on an alloy of zinc and antimony with dilute sulphuric acid (*see* nascent hydrogen, p. 9.).

(α.) $SbCl_3 + 3H_2 = SbH_3 + 3HCl$.
Antimonious chloride + Hydrogen = Stibine + Hydrochloric acid.

(β.) $Sb_2Zn''_3 + 6HCl = 2SbH_3 + 3HCl$.
Zinc antimony alloy + Hydrochloric acid = Stibine + Hydrochloric acid.

Properties.—A colorless, odorless, combustible gas forming when burnt, if the supply of air be free, antimonious oxide and water ($2SbH_3+3O_2=Sb_2O_3+3H_2O$), but if the supply of air be limited, the metal and water, the hydrogen only being in such case oxidized ($4SbH_3+3O_2=Sb_4+6H_2O$). A piece of cold porcelain held in the flame becomes rapidly coated with a black film of the metal. The gas is decomposed into its elements when passed through a red hot tube.

Passed into a solution of argentic nitrate a black precipitate of antimonious argentide is formed.

(N.B.—H_3As precipitates metallic silver).

$3AgNO_3 + SbH_3 = 3HNO_3 + SbAg_3$.
Argentic nitrate + Stibine = Nitric acid + Antimonious argentide.

From this reaction its composition as SbH_3 is inferred, the exact determination not being possible, owing to the gas having never been obtained free from hydrogen. SbH_3 being its composition, its rela-

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tionship to NH_3,PH_3, and AsH_3 becomes obvious. Moreover compounds of antimony with the alcohol-radicals, analogous to those formed by nitrogen, phosphorus and arsenic also exist, such as for example: trimethyl-stibine $Sb(CH_3)_3$, etc.

COMPOUNDS OF ANTIMONY AND OXYGEN.

Antimonious oxide (anhydride) ...	Sb_2O_3
Antimonious antimonate	Sb_2O_3,Sb_2O_5(=Sb_2O_4).
Antimonic oxide (anhydride) ...	Sb_2O_5.

(2.) Antimonious Oxide, *Trioxide, Sesquioxide, or Anhydride* (Sb_2O_3).

Natural History.—Found native as valentinite (white antimony ore; Sp. Gr. 5·56) and senarmontite.

Preparation.—(1.) By the combustion of metallic antimony in air or oxygen ($2Sb_2+3O_2=2Sb_2O_3$).

(2.) By digesting in a solution of sodic carbonate, the precipitate formed when a solution of antimonious chloride is poured into water.

$2SbCl_3$	+	$3Na_2CO_3$	=	Sb_2O_3	+	$3CO_2$	+	$6NaCl$.
Antimonious chloride	+	Sodic carbonate	=	Antimonious oxide	+	Carbonic anhydride	+	Sodic chloride.

Properties.—A dimorphous body, crystallising, like As_2O_3, both in needles, and in octahedra (*iso-dimorphous*). It is yellow when hot, and white (or buff-colored) when cold. It is fusible, volatile, and combustible, Sb_2O_4 constituting one of the products of its combustion.

It is soluble both in hydrochloric acid ($SbCl_3$ being formed) and in tartaric acid. With nitric acid it forms antimonic anhydride (Sb_2O_5). By the action of sulphuric acid upon it, an insoluble sulphate is produced. The *basic* properties of the oxide, however, are feeble. It is soluble in solutions of the fixed alkalies, and is hence called *antimonious acid*, and its salts *antimonites*.

It is soluble in a boiling solution of hydric-potassic tartrate or cream of tartar ($HKC_4H_4O_6$), forming the compound known as *tartar emetic* ($K,SbO,C_4H_4O_6$), which, unlike antimony salts generally, is both soluble in, and undecomposed by, water.

By ignition in hydrogen or with carbon, the oxide is reduced to the metallic state.

Uses.—As a substitute for white lead.

(3.) Antimonic Oxide, *Pentoxide* or *anhydride*, formerly called *Antimonic acid* (Sb_2O_5).

Preparation.—(1.) *As a hydrate*; (*Antimonic acid* Sb_2O_5,H_2O). By the action of nitric acid on antimony.

(2.) By decomposing antimonic chloride ($SbCl_5$) with water.

(3.) (*Anhydrous*). By heating the hydrate below redness.

Properties.—Antimonic oxide is white when cold and yellow when

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hot. At a strong heat it is converted into Sb_2O_4. It is insoluble both in water and in acids. It is soluble in, and forms definite compounds with, the alkalies.

Hydrates (Acids) of Antimonic Oxide.

Antimonic Acid ($H_2O,Sb_2O_5=HSbO_3$) is formed when antimony is treated with nitric acid ($Sb_2+4HNO_3=N_2O_3+2HSbO_3+N_2O_2+H_2O$). It is monobasic.

It forms salts as follows:—

(α.) *Normal salts*, $M'SbO_3(M'_2O,Sb_2O_5)$.*

(β.) *Acid salts*, $M'_2Sb_4O_{11}(M'_2O,2Sb_2O_5)$.

Metantimonic acid ($2H_2O,Sb_2O_5=H_4Sb_2O_7$) is formed when antimonic chloride is treated with water. It is bibasic. It forms salts as follows:—

(α.) *Normal salts*, $M'_4Sb_2O_7(2M'_2O,Sb_2O_5)$.

(β.) *Acid salts*, $M'SbO_3(2M_2O,2Sb_2O_5)$.*

The *Hydric-potassic metantimoniate* ($K_2H_2Sb_2O_7,6H_2O$) is used in the laboratory as a test reagent for sodium compounds, forming with them the insoluble (and the only insoluble sodium salt known) *hydric-sodic metantimoniate* ($Na_2H_2Sb_2O_7,6H_2O$). It should be remembered that the *normal* potassic antimoniate, into which the acid antimoniate rapidly passes, does not precipitate sodic salts.

(4.) Antimonious Antimoniate (Miller); *Diantimonic tetroxide* (Frankland); *Antimonoso-antimonic oxide* (Watts); ($Sb_2O_3,Sb_2O_5=Sb_2O_4$; $'Sb^{iv}{}_2O_4$).

Natural History.—It is found in nature as cervantite (*antimony ochre*).

Preparation.—(α.) By the ignition of antimonic oxide (Sb_2O_5), or (β.) by burning antimonious oxide (Sb_2O_3) in air.

(α.) $2Sb_2O_5 = 2Sb_2O_4 + O_2$

(β.) $2Sb_2O_3 + O_2 = 2Sb_2O_4$.

Properties.—A grey, infusible, non-volatile powder, insoluble both in water and in acids.

Its constitution is doubtful;—

(α.) Some regard it as (Sb_2O_3,Sb_2O_5) because (1) when treated with tartaric acid, Sb_2O_3 is dissolved, and Sb_2O_5 remains undissolved; and (2) that when its solution in hydrochloric acid is dropped into water, Sb_2O_3 is precipitated, and Sb_2O_5 remains dissolved.

(β.) Others regard it as Sb_2O_4, because it is soluble in alkalies without decomposition, forming salts called *antimonites* (*e.g.*, K_2O,Sb_2O_4; $K_2O,2Sb_2O_4$, etc.).

CHLORIDES OF ANTIMONY.

Antimonious chloride	...	...	$SbCl_3(\mathbf{Sb}Cl_3)$.
Antimonic chloride	...	...	$SbCl_5(\mathbf{Sb}Cl_5)$.

* N.B.—It will be noted that the acid metantimoniate is isomeric with the normal antimoniate.

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(5.) Antimonious Chloride; *Terchloride of antimony; Butter of antimony* ($SbCl_3$).

Preparation.—(1.) By distilling corrosive sublimate with antimony (or antimonious sulphide).

Sb_4	+	$4HgCl_2$	=	$2SbCl_3$	+	Sb_2Hg_2	+	Hg_2Cl_2.
Antimony	+	Mercuric chloride	=	Antimonious chloride	+	Antimony amalgam	+	Mercurous chloride.

(2.) By the action of hydrochloric acid on antimonious sulphide.

Sb_2S_3	+	$6HCl$	=	$3H_2S$	+	$2SbCl_3$.
Antimonious sulphide	+	Hydrochloric acid	=	Sulphuretted hydrogen	+	Antimonious chloride.

(3.) By the direct union of chlorine and the metal—

$$Sb_2 + 3Cl_2 = 2SbCl_3.$$

Properties.—A volatile, crystallizable, very deliquescent, and corrosive solid. It is fusible at 161·6° F. (72° C.), and volatile at higher temperatures. It boils at 433° F. (223° C.). It is soluble in hydrochloric acid and in a *little water*, but is decomposed by *a large excess of water*, an insoluble oxychloride or *powder of algaroth* being formed ($3SbCl_3 + 3H_2O = SbCl_3,Sb_2O_3$ (or $3SbClO$) $+ 6HCl$). By the long-continued action of water the oxychloride becomes antimonious oxide [$2(SbCl_3,Sb_2O_3) + 3H_2O = 6HCl + 3Sb_2O_3$].

Uses.—For bronzing gun-barrels to prevent rust. As a caustic.

(6.) Antimonic Chloride, *Pentachloride of antimony* ($SbCl_5$).

Preparation.—(1.) By acting on antimony with an excess of chlorine ($Sb_2 + 5Cl_2 = 2SbCl_5$).

(2.) By the action of chlorine on antimonious chloride ($SbCl_3 + Cl_2 = SbCl_5$).

Properties.—A colorless fuming liquid, having a suffocating odor. Mixed with a little water it forms white crystals of *antimonic oxy-trichloride* ($SbOCl_3$), but when treated with a quantity of water it forms *metantimonic acid* ($2SbCl_5 + 7H_2O = H_4Sb_2O_7 + 10HCl$). It absorbs sulphuretted hydrogen, forming the solid *antimonic chlorosulphide* (sulphotrichloride of Frankland) ($SbSCl_3$).

Use.—It is an active chlorinator, delivering up its chlorine with great ease.

The analogy of the compounds of phosphorus and of antimony with chlorine and oxygen may be noted here. Thus, $SbCl_3$ and $SbCl_5$ correspond to PCl_3 and PCl_5, whilst the chlorosulphide of antimony ($SbSCl_3$) corresponds to the chlorosulphide of phosphorus ($PSCl_3$).

Compounds of Antimony and Sulphur.

Antimonious sulphide	...	...	...	Sb_2S_3.
Antimonic sulphide	...	...	...	Sb_2S_5.

(10.) Antimonious Sulphide; *Tersulphide* or *Sesquisulphide of antimony; Sulphantimonious anhydride* (Frankland), ($Sb_2S_3 = 340$).

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Natural History.—It occurs in nature as stibnite (grey antimony ore; specific gravity 4·6).

Preparation.—(1.) By heating together (α) antimony and sulphur, or (β) antimonious oxide and sulphur—

(α.) $2Sb_2+3S_2=2Sb_2S_3$. (β.) $2Sb_2O_3+S_9=2Sb_2S_3+3SO_2$.

(2.) By passing sulphuretted hydrogen through a solution of antimonious chloride ($2SbCl_3+3H_2S=Sb_2S_3+6HCl$).

Properties.—The native compound is grey, brittle, crystalline (four-sided prisms), and fusible. The sulphide as precipitated by H_2S, is orange red (*antimony vermilion*), but becomes grey by heat, the change probably indicating its passage from an amorphous to a crystalline form.

In closed vessels it may be distilled unchanged, but when heated in open vessels it forms an *oxy-sulphide* ($Sb_2O_3,2Sb_2S_3=Sb_2S''_2O$), (antimonious oxy-disulphide: Frankland), which when fused constitutes what is called *glass of antimony*. "Red antimony ore" is a native oxy-sulphide. It is decomposed by hydrochloric acid ($Sb_2S_3+6HCl=3H_2S+2SbCl_3$).

Sulphantimonites.—When antimonious sulphide is acted on with an alkaline sulphide, or with an alkaline hydrate, it is dissolved, a soluble salt being formed, in which the alkaline sulphide constitutes the base, and antimonious sulphide the acid. This is known as a *sulphantimonite*. Thus—

$3K_2O$	+	$2Sb_2S_3$	=	Sb_2O_3	+	$3K_2S, Sb_2S_3$.
Potassic oxide	+	Antimonious sulphide.	=	Antimonious oxide.	+	Potassic sulphantimonite.

The solution, when concentrated, deposits a red powder, consisting of a variable mixture of sesquioxide and sesquisulphide of antimony (Kermes mineral). If an acid be added to the solution of this compound, Sb_2S_3 is precipitated.

The sulphantimonites are found native as lead, silver, copper, and iron salts.

(11.) Antimonic Sulphide; *Pentasulphide of antimony; Sulphantimonic anhydride; Sulphur auratum* (Sb_2S_5).

Preparation.—By passing sulphuretted hydrogen through a solution of antimonic chloride ($2SbCl_5+5H_2S=Sb_2S_5+10HCl$).

Properties.—An orange yellow body, decomposed by boiling in hydrochloric acid ($Sb_2S_5+6HCl=2SbCl_3+3H_2S+S_2$).

Sulphantimonates.—When antimonic sulphide is acted on either with the alkaline sulphides, or with the alkaline hydrates, a sulphantimonate is formed, the alkaline sulphide constituting the base, and the antimonic sulphide the acid. These compounds are analogous to the orthophosphates, as shown by their formula, viz.,—($3M_2S, Sb_2S_5$), or M_3SbS_4. The sodic sulphantimonate (Na_3SbS_4) is known as "*Schlippe's salt.*"

Tests for Antimony.—(*See* ANALYTICAL TABLES.)

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ARSENICUM (As=75).

Atomic weight, 75. *Molecular weight*, 300. *Specific gravity*, 5·9. *Atomicity, triad in arsenious compounds* (As_2O_3; $AsCl_3$), *and pentad in arsenic compounds* (As_2S_5; As_2O_5).

History.—Arsenic has been known from a very early date. The metal was first prepared by Brandt, in 1733.

Natural History.—It is found native, alloyed with other metals, as Co, Fe, Ni, etc. It sometimes occurs as a *sulphide* (*realgar*, As_2S_2), and as *orpiment* (As_2S_3), but is most often found in combination with metals as an *arsenide*, as *e.g.*, *kupfernickel* (NiAs) and $NiAs_2$; also as tin-white cobalt ($CoAs_2$). Frequently it is found as an arsenio-sulphide, as mispickel or arsenical pyrites (FeS_2,$FeAs_2$), or as cobalt glance (CoS_2,$CoAs_2$) or nickel glance (NiS_2,$NiAs_2$). It is found in some mineral waters, also in coal smoke, etc.

Preparation.—By reducing arsenious anhydride with charcoal ($As_2O_3+3C=As_2+3CO$).

Properties.—(*α.*) *Physical.* Arsenicum is a crystalline, brittle metal, having a brilliantly metallic steel-grey lustre. When heated to 356° F. (180° C.) it volatilises, without fusing. It is a conductor of electricity. The metal is not a poison until it becomes oxidised.

(*β.*) *Chemical.* When the dry metal is exposed to the air it undergoes no change, but when wetted and powdered it slowly oxidises, forming "fly-powder," which is probably a mixture of As and As_2O_3. Heated to 160° F. (71° C.) in air, it gives off condensible, colorless, garlic-smelling fumes of As_2O_3. At a red heat it burns with a white flame. It may be preserved unchanged in pure water. The powdered metal fires spontaneously when thrown into chlorine, its union with bromine, iodine, and sulphur, when heated, being also energetic. Nitric acid converts it into arsenic acid. Hydrochloric acid has no action upon it, unless it be mixed with potassic chlorate, when arsenic acid is formed. It is soluble in a solution of bleaching-powder.

Some chemists regard arsenicum as a non-metal. Their arguments in support of this view are its many analogies to phosphorus and nitrogen. Like the former, it burns spontaneously when placed in chlorine, and combines readily with sulphur and with the metals. Moreover it is capable of existing in various allotropic modifications, each possessing a different gravity. Others regard it as a *metal*, because of its high metallic lustre, its power of conducting electricity, its insolubility in common solvents, and its capability of forming alloys, whereby the properties of the metals with which it is associated are affected.

Uses.—For fly-powder, and in the manufacture of lead shot, to facilitate the lead assuming a globular form.

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Compounds of Arsenic.

		SALTS.	Formula (General.)	Formula (Constitutional.)	Molecular Weight.	Specific Gravity	As Per Cent.
1.	Hydrides.	Arsenious dihydride ..	H_4As_2 or As_4H_2	$'As''H_2$ / $'As''H_2$	154·0		97·40
2.	Hydrides.	Arseniuretted hydrogen (arsine)	H_3As	$As'''H_3$	78·0	2·695	96·15
3.	Oxides.	Arsenious anhydride (white arsenic) ..	As'''_2O_3	AsO / O / AsO	198·0		75·76
4.	Oxides.	Arsenic anhydride ..	As_2O_5	As_2O_5			65·22
5.	Sulphides.	Diarsenious disulphide (realgar)..	As_2S_2	$'As''_2S''_2$	214·0	3·5	70·09
6.	Sulphides.	Arsenious sesquisulphide (orpiment) ..	As_2S_3	$As_2S''_3$	246·0	3·5	60·97
7.	Sulphides.	Arsenic sulphide ..	As_2S_5	$As_2S''_5$	310·0		48·38
8.		Arsenious chloride ..	$AsCl_3$	$AsCl_3$	181·5	2·205	
9.		,, bromide ..	$AsBr_3$	$AsBr_3$		3·66	
10.		,, iodide ..	AsI_3	AsI_3	456·0	4·39	
11.		,, trifluoride..	AsF_3	AsF_3			
12.		,, pentafluoride (not known in a free state)	AsF_5				

Compound of Arsenic and Hydrogen.

Arseniuretted hydrogen ... ... AsH_3.

(2.) Arseniuretted (or **Arsenetted**) **Hydrogen.**—*Arsenious hydride; arsine; trihydride of arsenic* (H_3As).

History.—Discovered by Scheele (1755).

Preparation.—By acting either (α) on a mixture of zinc and arsenious acid or (β) on an alloy of zinc and arsenicum, with dilute sulphuric acid (nascent hydrogen).

(α.) $As_2O_3 + 6Zn + 6H_2SO_4 = 2AsH_3 + 6ZnSO_4 + 3H_2O$.

(β.) $As_2Zn''_3 + 3H_2SO_4 = 3ZnSO_4 + 2AsH_3$.

Properties.—(α.) *Sensible and physical.* A colorless, garlic-smelling, intensely poisonous gas (Sp. Gr. 2·695). It is slightly soluble in water. It becomes liquid at — 22° F. (— 30° C.), but has never been solidified. It is decomposed by passage through a hot tube ($AsH_3 = As_2 + 3H_2$).

(β.) *Chemical.* Its reaction is neither acid nor alkaline. It burns with a bluish-white flame, forming water and arsenious anhydride if the supply of air be free ($2AsH_3 + 3O_2 = As_2O_3 + 3H_2O$), or water and the metal if the supply be limited ($4AsH_3 + 3O_2 = As_4 + 6H_2O$). The flame deposits metallic arsenic on bodies placed within it, and arsenious anhydride on bodies placed above it. It is decomposed by chlorine, hydrochloric acid and the solid hydride (As_4H_2 ?) being formed.

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The gas is absorbed by *nitric acid*, arsenic acid being produced; also by *cupric sulphate*, an arsenide of copper being precipitated ($2AsH_3+3CuSO_4=3H_2SO_4+As_2Cu_3$); and also by *argentic nitrate*, arsenic acid being formed, and silver precipitated ($AsH_3+6AgNO_3+3H_2O=6HNO_3+H_3AsO_3+3Ag_2$). The gas is also absorbed by a solution of corrosive sublimate, and by oil of turpentine. Chemically, it is closely related to ammonia and to phosphoretted hydrogen, all three gases being inflammable, possessing a peculiar smell, being decomposed by heat, and being formed by the action of nascent hydrogen on their corresponding oxygen compounds (*viz.*, N_2O_3; P_2O_3; Cu_2O_3).

(1.) The *solid hydride* (H_4As_2 (Soubeiran) or As_4H_2 (Wiederhold),) is a brown solid, and is formed either when a plate of arsenicum is used as the negative pole in the electrolysis of water, or when sodium arsenide is decomposed with water. It burns in air.

(3.) Arsenious Anhydride; *Arsenious acid; Arsenic trioxide; White arsenic; Arsenic* (As_2O_3). — *Arsenious acid* ($H_3AsO_3=As_2O_3,3H_2O$). (The acid is only known in solution.)

Natural History.— Arsenic is found native as arsenite.

Preparation.—Either (1) by roasting arsenical ores in a current of air, or (2) by heating arsenicum in air.

Properties.—(a.) *Physical.*—Arsenicum exists in two forms. (1.) A *vitreous form* (specific gravity 3·738), which is transparent and colorless when first prepared, but becomes opaque, yellowish-white, and somewhat like porcelain, after exposure to air. Some doubt exists as to the true cause of this change. (2.) A *crystalline form* (octahedra), (specific gravity 2·695), which arsenic assumes when carefully sublimed in small quantities, or when crystallized from a hydrochloric acid solution.

Arsenic is very nearly, if not entirely, destitute both of taste and smell. The opaque variety has a lower specific gravity than the transparent. Heat converts the opaque form into the vitreous, whilst mere grinding in a mortar converts the vitreous into the opaque. Heated to 380° F. (193° C.), it softens and sublimes without fusing, forming transparent octahedral crystals on warmed surfaces. A somewhat characteristic behaviour of arsenic is the white layer that it forms on the surface of water when the arsenic is thrown into it in a state of powder, the particles of arsenic repelling the water and collecting round the air bubbles.

The solubility of arsenic in water is a question of very considerable importance. The following are the chief circumstances that serve to modify the dissolving action of water on the acid:—

1. The peculiar modification of acid used.

2. Its admixture or contamination with organic matter. It is said that the presence of greasy matter, such as bacon, reduces the solubility of arsenious acid to one-twentieth. If this be the fact, it affords a partial explanation, why sometimes its action on the human body

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seems to be suspended.—(Dr. Blondlot, "Medical Times and Gazette," Feb. 11, 1860.)

3. The length of time the water has acted.
4. The temperature of the water.
5. If boiled, the length of time that the boiling has been continued.
6. The time that elapses between boiling and the examination.

We will endeavour to state a few results we have obtained, in a tabular form:—

Solubility of Arsenious Acid.

	Transparent form.	Opaque form.	Fresh crystalline acid.
1000 grains of cold distilled water, after standing for 24 hours, dissolved ..	1·74 grains.	1·16 grains.	2·0 grains.
1000 grains of boiling water poured on the acid, and allowed to stand for 24 hours, dissolved	10·12 ,,	5·4 ,,	15·0 ,,
1000 grains of water boiled for one hour, the quantity being kept uniform by the addition of boiling water from time to time, and filtered immediately, dissolved	64·5 ,,	76·5 ,,	87·0 ,,

(β.) *Chemical Properties.*—Arsenious acid, when in solution, has a feebly acid reaction; but it readily combines with bases, the salts being called *arsenites*. It does not neutralize the alkalies, nor does it decompose alkaline carbonates unless heated. The arsenites generally are easily decomposed by a stronger acid. The arsenites of the alkalies are soluble in water, and are very poisonous. The other arsenites are almost insoluble; hence the action of lime and magnesia as antidotes. Most of the arsenites are decomposed by heat, whilst all, when heated with a reducing agent, evolve the metal in a vaporous form. The copper arsenite, or Scheele's green (*see* page 372), and the silver arsenite are the two most important salts.

Arsenious acid is readily soluble in solutions of the fixed caustic alkalies, but is not very soluble in ammonia. It is very slightly soluble in sulphuric acid, but is freely soluble in hot nitric acid, the arsenious being changed to arsenic acid. It is also readily soluble in hydrochloric and in some vegetable acids, in alcohol (1 in 2000 of alcohol of specific gravity 0·802), and in chloroform (1 in 200,000), but is insoluble in absolute ether. When chlorine is passed through a solution of the acid, arsenic acid is formed.

Uses.—In the manufacture of glass. The solutions of the arsenites of potash and soda are used as sheep-dipping compositions. An arsenical soap (camphor, soap, and arsenite of potash) is used as a preservative for the skins of animals. Arsenite of soda is used as a means of preventing the incrustation of boilers. Arsenite of copper

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(*Scheele's green*) is used as a pigment for paper-hangings, feathers, muslins, etc. Arsenic and arsenite of potash (Fowler's solution) are used in medicine.

(4.) **Arsenic Anhydride** (As_2O_5). — *Arsenic Acid*, $H_3AsO_4 = As_2O_5,3H_2O$.

Preparation.—By oxidizing arsenious anhydride with nitric acid ($As_2O_3 + 2HNO_3 + 2H_2O = N_2O_3 + As_2O_5,3H_2O$).

Properties.—*Physical.* A white deliquescent solid, soluble in water. When heated it is decomposed ($As_2O_5 = As_2O_3 + O_2$).

Chemical. As an acid it is more powerful than arsenious acid. The solution of the acid, when allowed to stand, deposits crystals having the composition $As_2O_5,3H_2O$, *aq.* At 212° F. (100° C.) the crystals melt, and lose their water of crystallization, becoming $As_2O_5,3H_2O$. Heated to 320° F. (160° C.) it becomes $As_2O_5,2H_2O$ ($=H_4As_2O_7$, pyro-arsenic acid). At 392° F. (200° C.), it becomes As_2O_5,H_2O ($=HAsO_3$ met-arsenic acid), and at 500° F. (260° C.) As_2O_5 only is left.

Arsenic acid is tribasic (H_3AsO_4). It forms salts called *arsenates*, which closely resemble, and are isomorphous with, the tribasic phosphates.

Uses.—Arsenic acid is used in the preparation of magenta by its action on aniline. *Arsenate of soda* is used by the calico-printers as a dung substitute.

Compounds of Arsenic and Sulphur.

Diarsenious Disulphide	As_2S_2.
Arsenious Sesquisulphide	As_2S_3.
Arsenic Sulphide	As_2S_5.

(5.) **Diarsenious Disulphide;** *Realgar.* (As_2S_2 or $'As''_2S''_2$) is found native.

Preparation.—By heating together sulphur and arsenious anhydride ($2As_2O_3 + S_7 = 2As_2S_2 + 3SO_2$).

Properties.—A red, transparent, fusible, and volatile solid, burning with a blue flame, sulphurous and arsenious anhydrides (SO_2 and As_2O_3) forming the products of combustion. It is insoluble in water and in hydrochloric acid; but is soluble in nitric acid (forming arsenic and sulphuric acids), also in aqua regia and in potassic disulphide. It is decomposed by the fixed alkalies, leaving, as a precipitate, a brown arsenical subsulphide ($As_{12}S$). It is used in the manufacture of fireworks.

(6.) **Arsenious Sesquisulphide;** *Tersulphide of Arsenic; Sulpharsenious [acid] anhydride; orpiment* (As_2S_3).

Natural History.—Found native.

Preparation.—(1.) By passing sulphuretted hydrogen through a solution of arsenious acid acidulated with hydrochloric acid.

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$3H_2S$	+	$2AsCl_3$	=	$6HCl$	+	As_2S_3.
Sulphuretted hydrogen	+	Arsenious chloride	=	Hydrochloric acid	+	Arsenious sesquisulphide.

(2.) By subliming a mixture of sulphur and arsenious anhydride.

S_9	+	$2As_2O_3$	=	$2As_2S_3$	+	$3SO_2$.
Sulphur	+	Arsenious anhydride	=	Arsenious sesquisulphide	+	Sulphurous anhydride.

Properties.—A yellow, crystalline, fusible, and volatile substance (Specific gravity 3·5), insoluble in water and in dilute acids. It is decomposed by nitric acid and by aqua regia. It burns in air, but may be sublimed in closed vessels. It is a feeble sulphur acid. It is soluble in ammonic carbonate and also in the alkalies, an alkaline arsenite and sulpharsenite being formed.

$12KHO$	+	$2As_2S_3$	=	$3K_2S,As_2S_3$	+	$3K_2O,As_2O_3$	+	$6H_2O$.
Potassic hydrate	+	Arsenious sesquisulphide	=	Potassic sulph-arsenite	+	Potassic arsenite	+	Water.

On adding an acid to the solution, an arsenious sulphide (As_2S_3) is reprecipitated.

Uses.—It is used as a pigment (King's yellow). The ammoniacal solution is used for dyeing, the color being deposited as the ammonia evaporates.

(7.) **Arsenic Sulphide**; *Diarsenic pentasulphide; Sulpharsenic acid* (As_2S_5).

Preparation.—(1.) By fusing together a mixture of sulphur and orpiment.

(2.) (α.) By passing sulphuretted hydrogen through a solution of sodic arsenate, a solution of *sulph-arsenate of sodium* is formed.

(β.) When hydrochloric acid is added to this solution *arsenic sulphide* is precipitated. These reactions are seen in the following equations:—

(α.)	$2Na_2O,H_2O,As_2O_5$	+	$7H_2S$	=	$8H_2O$	+	$2Na_2S,As_2S_5$.
	Sodic arsenate	+	Sulphuretted hydrogen	=	Water	+	Sodic sulpharsenate.

(β.)	$2Na_2S,As_2S_5$	+	$4HCl$	=	$4NaCl$	+	$2H_2S$	+	As_2S_5.
	Sodic sulpharsenate	+	Hydrochloric acid	=	Sodic chloride	+	Sulphuretted hydrogen	+	Arsenic sulphide.

Properties.—A yellow, volatile, fusible substance, solidifying after fusion to an orange-colored glass. It is one of the most powerful of the sulphur acids. It forms salts analogous to the phosphates called *sulph-arsenates* ($M'AsS_3$ *meta-sulpharsenate*; $M_4As_2S_7$ *pyro-sulpharsenate*; M_3AsS_4 *ortho-sulpharsenate*).

(8.) **Arsenious Chloride**; *Terchloride of arsenic* ($AsCl_3$).

Constitution.—Half a volume of arsenic vapor + 3 volumes of Cl = 2 volumes of $AsCl_3$ (specific gravity of vapor 6·3).

Preparation.—(1.) By burning the metal in chlorine.

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(2.) By passing dry chlorine over heated arsenious anhydride.

$$11As_2O_3 + 6Cl_2 = 4AsCl_3 + 3(2As_2O_3,As_2O_5).$$

Arsenious anhydride + Chlorine = Arsenious chloride +

(3.) By distilling together arsenious anhydride and mercuric chloride.

Properties.—A heavy (specific gravity 2·2), pungent, oily, volatile, fuming liquid, boiling at 269·6° F. (132° C.), and remaining fluid at —20·2° F. (—29° C.). It is decomposed when treated with a quantity of water ($2AsCl_3+3H_2O=As_2O_3+6HCl$), but with a little water, it forms crystals of the oxychloride (AsClO).

(9.) Arsenious Bromide is prepared in a similar manner to the chloride. It is a fusible crystalline body.

(10.) Arsenious Iodide is prepared similarly to the chloride and bromide. It is a crystalline orange-colored body. It is not decomposed by water.

Reactions of Arsenicum Compounds.—*See* ANALYTICAL TABLES.

GOLD (*Aurum*) (Au).

Atomic weight, 196·7. *Molecular weight* (*probable*), 393·4. *Specific gravity*, 19·4. *Fuses at from* 2012° F. *to* 2192° F. (1100° C. *to* 1200° C.). *Atomicity, monad* (′) *as in aurous compounds* (AuCl; Au_2O), *and triad* (‴) *as in auric compounds* ($AuCl_3$; Au_2O_3).

History.—Known to the ancients (☉ Sol).

Natural History.—It is always found in the metallic state. It occurs as cubes or octahedra in the alluvial sands of certain rivers (gold dust), and also in masses in certain volcanic rocks (nuggets). It is, moreover, always found alloyed with silver, frequently with copper, and sometimes with osmium, iridium, antimony and tellurium.

Extraction.—(1.) *Process of washing.* This consists in treating the well-powdered ore with water, whereby the sand is mechanically washed away from the gold, owing to the different gravities of the sand and the metal.

(2.) *Process of amalgamation.* This consists in dissolving out the gold, with mercury from the *débris* with which it is associated, the quicksilver being afterwards separated from the gold by distillation.

(3.) Sometimes the gold ore is fused with a mixture of metallic lead, lime, and oxide of iron. The lead in a state of fusion dissolves the gold, the liquid alloy sinking to the bottom of the slag. The gold is afterwards separated from the lead by cupellation (*see* page 411.)

Preparation of pure gold.—Dissolve the gold in aqua regia ($1HNO_3$ and 4HCl), and add ferrous sulphate. This will become oxidised to ferric sulphate, whilst the gold will be precipitated, the precipitate appearing brown by reflected, but purple by transmitted light $6FeSO_4+2AuCl_3=2(Fe_23SO_4)+Fe_2Cl_6+Au_2$.

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This precipitate is now boiled with hydrochloric acid, whereby all silver and iron are removed. The pure precipitated metal is then fused with hydric potassic sulphate.

Properties.—(*α.*) *Physical.* A soft, heavy, yellow metal, possessing great lustre (Sp. Gr. 19·4). It is the most ductile and malleable metal known, and is also one of the most perfect conductors of heat and electricity. It fuses at 1899° F. (1037° C.), shrinking greatly in bulk as it solidifies. It is volatile at the heat of the oxy-hydrogen jet, giving off a purple vapor. A very fine gold leaf is transparent to the green rays of light.

(*β.*) *Chemical.* Gold is unaffected at any temperature either by air or moisture. Sulphuretted hydrogen is without action upon it. It is soluble in aqua regia, or in any mixture which, like aqua regia, liberates chlorine; but it is insoluble either in any simple acid (except selenic acid), or in solutions of the alkalies. It combines readily with phosphorus by heat, and with the haloids in the cold.

Uses.—For *coinage*, mixed with 8·33 per cent. of copper, to increase its hardness. For *jewellery:* pure gold is regarded as of 24 carats; English standard gold of 22 carats (that is, 22 parts of gold in every 24). An 18 carat gold contains $\frac{18}{24}$ or $\frac{3}{4}$ its weight of gold. Gold is also used for *gilding;* for coloring glass ruby red; for gold leaf, wire, etc.

Compounds of Gold.

	SALTS.	Formula (General).	Formula (Constitutional).	Molecular Weight.	Au per cent.
1.	Oxides — Aurous oxide or suboxide	Au_2O	Au_2O	409·4	
2.	Oxides — Auric oxide or peroxide, or auric anhydride ..	Au_2O_3	$\left\{\begin{matrix}AuO\\O\\AuO\end{matrix}\right.$	441·4	
3.	Chlorides — Aurous chloride	AuCl	AuCl	232·2	
4.	Chlorides — Auric chloride .. .. (Iodides correspond to chlorides.)	$AuCl_3$	$AuCl_3$	303·2	64·86
5.	Sulphides — Aurous sulphide	Au_2S	Au_2S''	425·4	
6.	Sulphides — Auric sulphide	Au_2S_3	$\left\{\begin{matrix}AuS''\\S''\\AuS''\end{matrix}\right.$	489·4	

Compounds of Gold and Oxygen.

Aurous oxide	Au_2O.
Auric oxide	Au_2O_3.

(1.) Aurous Oxide; *Suboxide of gold* (Au_2O).

Preparation.—Precipitated on adding a dilute solution of potassic hydrate to one of aurous chloride.

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Properties.—A dark powder, soluble in an excess of alkali. It rapidly decomposes into auric oxide and the metal.

(2.) Auric Oxide; *Peroxide* or *Sesquioxide of gold; Auric anhydride* (Au_2O_3=441·2).

Preparation.—A solution of auric chloride is decomposed by magnesia, a magnesic aurate being precipitated. This magnesic aurate is then digested with nitric acid, when an insoluble auric oxide remains, either as a yellow hydrate ($Au_2O_3,3H_2O$), or as a brown precipitate (Au_2O_3), the exact compound formed being dependent on the strength of the nitric acid employed.

Properties.—By exposure to light, or by a heat of 473° F. (245° C.), auric oxide is resolved into the metal and oxygen. With the alkalies, the hydrated oxide forms soluble salts, called *the aurates*, as, *e.g.*, *potassic aurate* ($KAuO_2,3H_2O$), a compound used by electro-gilders. With the earths, and with other metallic oxides, it forms insoluble compounds. With ammonia, it forms "fulminating gold"—($Au_2O_3,4NH_3,H_2O$).

Strong nitric and sulphuric acids dissolve it, the oxide being deposited on dilution. With HCl, HI, and HBr, it forms $AuCl_3$, AuI_3, and $AuBr_3$.

COMPOUNDS OF GOLD AND CHLORINE.

Aurous chloride	AuCl.
Auric chloride	$AuCl_3$.

(3.) Aurous Chloride; *Protochloride of gold* (AuCl=232·1).

Preparation.—By heating auric chloride to 347° F. (175° C.), until chlorine ceases to be evolved.

Properties.—An insoluble yellow substance, decomposed at 390° F. (200° C.). By the action of boiling water, or by mere exposure to light, it is converted into the metal and $AuCl_3$.

(4.) Auric Chloride; *Terchloride of gold* ($AuCl_3$=303·1).

Preparation.—(1.) By dissolving gold in aqua regia and evaporating the solution at 248° F. (120° C.).

(2.) By heating gold-leaf in a current of chlorine.

Properties.—A red, deliquescent, crystalline mass. Heated to 390° F. (199° C.), it becomes AuCl; but when heated above this temperature, it is entirely decomposed. It is soluble in water, in alcohol, and in ether, the latter solvent being capable of removing it from its aqueous solution. Its solution in water stains the skin and other organic matter purple, finely divided gold being deposited. The extreme ease with which the gold of the salt may be reduced, renders it useful in photography.

It forms crystallizable compounds with the alkaline chlorides, and with the chlorides of most organic bases. With ammonia, it forms "*fulminating gold.*"

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Purple of Cassius. — When a dilute solution of stannous and stannic chloride is added, drop by drop, to a very dilute neutral solution of auric chloride, a purple precipitate is gradually thrown down, the subsidence of which is aided by the presence of a soluble salt and heat. This precipitate is called "*the purple of Cassius*" ($Sn''Au_2Sn_2O_6,4H_2O(?)$, *i. e.*, a double stannate of gold and tin). It may also be prepared by digesting metallic tin in a neutral solution of auric chloride. It is soluble in ammonia, the solution being decomposed and rendered colorless by light, metallic gold being precipitated. The precipitate, mixed with a little borax, is employed for coloring china and porcelain a rich rose red. The color is a mixture of metallic gold and stannic oxide.

COMPOUNDS OF GOLD AND SULPHUR.

Aurous sulphide	Au_2S.
Auric sulphide	Au_2S_3.

(5.) Aurous Sulphide (Au_2S or Au_2S'').

Preparation.—By passing sulphuretted hydrogen through a *boiling* solution of auric chloride.

Properties.—A black substance, soluble in the alkaline sulphides.

(6.) Auric Sulphide (Au_2S_3).

Preparation.—By passing sulphuretted hydrogen through a *cold* dilute solution of auric chloride.

Properties.—A yellow substance, soluble in the alkaline sulphides.

A soluble *double sulphide of gold and potassium* may be prepared by heating together gold, sulphur, and potassic carbonate. It resists a red heat, and is used for gilding china (*Burgos lustre*).

Reactions of the Compounds of Gold.

1. Heated in the open air, all gold salts are reduced.
2. *Ferrous sulphate* gives in acid solutions (free nitric acid being absent) a brown ppt. of metallic gold.
3. *A mixture of dilute stannous and stannic chloride* (or metallic tin), gives in a neutral solution a ppt. of "purple of Cassius."
4. *Mercurous nitrate* also gives a dark brown ppt. of reduced gold.
5. *Sulphuretted hydrogen*, a black ppt. (Au_2S_3) in a boiling solution.

Estimation.—Gold is estimated as the metal, precipitated by ferrous sulphate.

PLATINUM (Pt.)

Atomic weight, 197·4. *Specific gravity*, 21·5. *Atomicity: a dyad in platinous salts, e. g.* ($Pt''Cl_2$), *and a tetrad in platinic salts* ($Pt^{iv}Cl_4$).

History.—Discovered by Wood, of Jamaica, 1741.

Natural History.—It occurs native in the *débris* of the older volcanic rocks in small grains, alloyed with palladium, rhodium,

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iridium, osmium and ruthenium; and sometimes also in larger nodules, alloyed with gold, silver, copper, iron, and lead.

Extraction.—(1.) The ore is first dissolved in aqua regia, a solution of platinic chloride ($PlCl_4$) being formed. Ammonic chloride is now added to the clear filtrate, by which means the platinum is precipitated as a double chloride of platinum and ammonium ($2NH_4Cl,PtCl_4$). This precipitate is now heated, when the ammonia and the chlorine are expelled, and the metal left in the spongy condition. This spongy mass is now powdered, and the powder forcibly compressed into a solid block. This block is then intensely heated, and hammered whilst hot, so as to weld the metallic particles together into a solid lump (process of Wollaston).

Deville and Debray have suggested to fuse the metal in a lime crucible by the oxy-hydrogen blowpipe, instead of effecting the union of the metallic particles by welding. All impurities, except rhodium and iridium are in this way removed, the gold and the palladium being volatilized in the metallic state, the sulphur, phosphorus, arsenic and osmium being volatilised as oxides, whilst the iron and copper are first oxidised and afterwards absorbed by the lime crucible.

(2.) Another process suggested by Deville and Debray is as follows:—The platinum ore is roasted with lead sulphide and oxide, when the reduced lead dissolves the platinum (together with some iridium and rhodium) an easily fusible alloy being formed, whilst an alloy of iridium and osmium (osmide of iridium), which is insoluble in the melted lead, sinks to the bottom of the platiniferous lead. The alloy of lead and platinum is then ladled away from the insoluble residue, and the lead removed by cupellation from its alloy with the platinum. The crude platinum is afterwards refined by fusion with the oxy-hydrogen blowpipe. It still, however, retains iridium and rhodium. These metals are said to improve rather than to injure the platinum for the purposes of chemical apparatus.

In preparing "platinum black," platinous chloride ($PtCl_2$) is dissolved in a solution of potassic hydrate, and heated with alcohol. The precipitated platinum black is then collected, washed and dried.

Properties.—(*a.*) *Physical.* A white hard metal, of great tenacity. It cannot be crystallised artificially, although native octahedra have been met with. Its specific gravity varies from 21 to 22, according to the process by which it is prepared. It expands very slightly by heat; hence platinum wires may be sealed into glass. It may be fused by the oxy-hydrogen blow-pipe, or by the galvanic battery. Its conducting power for heat and electricity is very inferior to that of either silver or gold.

(*β.*) *Chemical.* Platinum does not oxidise in the air at any temperature, but, like silver, it absorbs oxygen mechanically when heated, evolving it again on cooling. It is unacted upon by any acid except nitro-hydrochloric acid. It corrodes when heated with the caustic

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alkalies, or with the alkaline earths. At high temperatures it is easily attacked by carbon, phosphorus, boron, silicon, etc. It possesses in all its forms, but more especially in the spongy condition (platinum black), a remarkable power of inducing chemical combination between oxygen and other gases (*see* page 9).

Uses.—In the laboratory it is largely employed, because of its infusibility, and also its power of resisting chemical reagents (*e.g.*, oil of vitriol stills, etc.).

Compounds of Platinum.

	SALTS.	Formula (General).	Formula (Constitutional).	Molecular Weight.	Specific Gravity.	Pt per cent.
Chlor-ides.	Platinous oxide..	PtO	**Pt**O	213·4		
Ox-ides.	Platinic oxide ..	PtO_2	**Pt**O_2	229·4		
Chlor-ides.	Platinous chloride	$PtCl_2$	**Pt**Cl_2	268·4		
	Platinic chloride	$PtCl_4$	**Pt**Cl_4			Pt 58·12
	Potassic platino-chloride..	$2KCl,PtCl_4$	$2\mathbf{K}Cl,\mathbf{Pt}Cl_4$	488·3	3·586	Pt 40·36 K 16·02=K_2O 19·29
	Sodic-platino-chloride ..	$2NaCl,PtCl_4$	$2\mathbf{Na}Cl,\mathbf{Pt}Cl_4$			
	Ammonic platino-chloride..	$2H_4NCl,PtCl_4$	$2\mathbf{N}H_4Cl,\mathbf{Pt}Cl_4$	446·4	3·009	Pt 44·18 H_3N 7·62
	[Bromides and iodides analogous to chlorides.]					
Sul-phides.	Platinous sulphide	PtS	**Pt**S″			
	Platinic sulphide	PtS_2	**Pt**S''_2			
Oxy-salts.	Platinic sulphate	$Pt(SO_4)_2$				
	Platinic nitrate..	$Pt(NO_3)_4$				
	Platinous sulphite	$PtSO_3$				

Compounds of Platinum and Oxygen.

1. Platinous oxide... ... ... PtO.
2. Platinic oxide ... ... PtO_2.

(1.) Platinous Oxide.—*Monoxide* or *protoxide* (PtO=213·1).

Preparation.—By decomposing platinous chloride with a solution of potassic hydrate, and afterwards neutralising with sulphuric acid.

Properties.—A black substance, easily decomposed by heat. It acts as a feeble base, being soluble in acids as well as in an excess of an alkali.

(2.) Platinic Oxide.—*Binoxide of platinum* (PtO_2=229·4).

Preparation.—(*As a hydrate,* $PtO_2,2H_2O$.) By adding sodic carbonate to a solution of platinic nitrate. [Only one-half of the total quantity

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of sodic carbonate necessary for complete precipitation should be added, because of the tendency of PtO_2 to combine with alkaline bases.]

Properties.—The hydrate is brown, and the anhydrous oxide black. All the oxygen may be expelled from the oxide by heat. It is a weak base, the salts being yellowish-red. Occasionally it acts as an acid (platinic acid), as, for example, in *platinate of soda* ($Na_2O,3PtO_2,6H_2O$).

Compounds of Platinum and Chlorine.

1. Platinous chloride	...	...	...	$PtCl_2$.
2. Platinic chloride	...	...	...	$PtCl_4$.

(3.) Platinous Chloride.—*Protochloride of platinum* ($PtCl_2$=268·4).

Preparation.—(1.) By evaporating a solution of platinum in aqua regia to dryness, and heating the residue at 455° F. (235° C.), until chlorine ceases to be evolved.

Properties.—An olive-green powder, soluble in potassic hydrate, in hot hydrochloric acid (the solution being red), and in platinic chloride (the solution being brown); insoluble in water, or in nitric or sulphuric acids. Heat decomposes it. With the alkaline chlorides it forms double salts called *chloro-platinites*, or *platinoso-chlorides*.

(4.) Platinic Chloride.—*Tetrachloride, perchloride* or *bichloride of platinum* ($PtCl_4$=339·4).

Preparation.—By dissolving platinum in aqua regia, and evaporating to dryness.

Properties.—A red-brown, crystalline, deliquescent salt, soluble in alcohol, in ether, and in water, the aqueous solution being of a deep orange color. Heated to 455° F. (235° C.) it becomes $PtCl_2$, but when heated beyond this it is entirely reduced. Sulphurous acid reduces it to $PtCl_2$. With metallic chlorides it forms double salts called *chloro-platinates*, or *platino-chlorides*. The potassic and ammonic platino-chlorides ($2KCl,PtCl_4$ and $2(NH_4Cl),PtCl_4$) are only slightly soluble in water, and quite insoluble in alcohol. They constitute, therefore, a means of estimating the ammonium or the potassium present in a solution. Both the potassic and ammonic platino-chlorides consist of yellow octahedral crystals. The ammonium salt is easily decomposed by heat, but the potassium salt is decomposed with difficulty. The sodium compound is, on the contrary, of a red color, and very soluble both in water and in alcohol. Platinic chloride also forms double salts with the chlorides of some of the organic bases.

Bases Produced by the Action of Ammonia on the Chlorides of Platinum.

These bases are to be regarded as ammonias, in which a part of the hydrogen of two or more ammonia molecules has been displaced either by platinosum (Pt'') or by platinicum (Pt^{iv}).

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(1.) **Diplatosamine** (*hydrated*), *Reiset's first base*; [$Pt''H_{10}N_4,2H_2O$, or $\left.\begin{matrix}H_4\\H_4\\Pt''H_2\end{matrix}\right\}N_4,2H_2O$].

On adding an excess of ammonia to a boiling hydrochloric acid solution of platinous chloride, a green precipitate is deposited (*green salt of Magnus*; $Pt''Cl_2(NH_3)_2$ or $\left.\begin{matrix}N_2H_6\\Pt''\end{matrix}\right\}Cl_2$). Of this salt there are also yellow and red isomers.

The *hydrochlorate of diplatosamine* ($Pt''H_{10}N_4,2HCl,H_2O$) is formed on heating "the green salt of Magnus" with an excess of ammonia.

The *sulphate of diplatosamine* ($Pt''H_{10}N_4H_2SO_4$) is formed when argentic sulphate is added to a solution of the hydrochlorate.

The hydrated base *diplatosamine* ($Pt''H_{10}N_4,2H_2O$) is formed by acting on a solution of the sulphate with baric hydrate.

This base is a strong, caustic, deliquescent alkali, and like the alkaline hydrates, both absorbs carbonic acid from the air, and expels ammonia when added to its salts.

[Nitrous acid gives with the salts of diplatosamine a blue or green precipitate or coloration.]

(2.) **Platosamine** (*hydrated*), *Reiset's second base* [$Pt''H_4N_2,H_2O$ or $\left.\begin{matrix}H_2\\H_2\\Pt''\end{matrix}\right\}N_2,H_2O$].

This is prepared by heating the hydrate of diplatosamine to 230° F. (110° C.) so long as it gives off water and ammonia. It acts as a base, forming insoluble but easily decomposed salts with acids.

The hydrochlorate of platosamine may be produced by heating the hydrochlorate of diplatosamine until it ceases to give off water and ammonia. Thus—

$$\underset{\text{Hydrochlorate of diplatosamine}}{Pt''H_4N_4,2HCl,H_2O} + \textit{heat} = \underset{\text{Hydrochlorate of platosamine.}}{Pt''H_4N_2,2HCl} + \underset{\text{Water}}{H_2O} + \underset{\text{Ammonia.}}{2NH_3}.$$

(3.) **Platinamine** (*hydrated*), *Gerhardt's base* ($Pt^{iv}H_2N_2,4H_2O$ or $\left.\begin{matrix}H_2\\Pt^{iv}\end{matrix}\right\}N_2,4H_2O$).

The *hydrochlorate of platinamine* ($Pt^{iv}H_2N_2,4HCl$) is formed by passing chlorine through hydrochlorate of platosamine suspended in boiling water.

The *nitrate of platinamine* ($Pt^{iv}H_2N_2,4HNO_3$) is formed by boiling the hydrochlorate of platinamine with argentic nitrate.

The hydrated base *platinamine* ($Pt^{iv}H_2N_2,4H_2O$) is formed on adding ammonia to a boiling solution of the nitrate. It has the same composition as that assigned to *fulminating platinum*.

Other platinum compounds derived from ammonia, such as the salts of Gros and Raewsky, are known. They are believed to be com-

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pounds of the base diplatinamine ($Pt^{iv}H_8N_4,2H_2O$), although the base itself has not, as yet, been isolated.

Compounds of Platinum and Sulphur.

(1.) Platinous sulphide... ... ... PtS.
(2.) Platinic sulphide ... ... PtS_2.

(8, 9.) These sulphides are formed by the action of sulphuretted hydrogen on platinous and platinic chlorides respectively. Platinic sulphide is soluble in the alkaline sulphides and hydrates, forming the *sulpho-platinates.*

Reactions of Platinum Compounds.
Platinic Salts.

1. *Sulphuretted hydrogen;* a black ppt., soluble in excess of ammonic sulphide.
2. *Ammonia;* a yellow ppt. ($2NH_4Cl,PtCl_4$), decomposed by heat.
3. *Potassic hydrate;* a yellow ppt. ($2KCl,PtCl_4$).
4. *Stannous chloride;* a deep brown in acid solutions.
5. *Potassic iodide;* a brown ppt. of PtI_4.

Estimation of Platinum.—(1.) As a metal.
(2.) As a potassic or ammonic platinic chloride—

100 ($2KCl,PtCl_4$) = 40·36 Pt.
100 ($2NH_4Cl,PtCl_4$) = 44·18 Pt.

MOLYBDENUM (Mo).

Atomic weight, 96. *Atomicity; dyad in molybdous compounds* (*as* $MoCl_2$, MoO), *and tetrad in molybdic compounds* (MoO_2, $MoCl_4$).

Natural History.—It occurs chiefly as a *disulphide* (called molybdena (*μολύβδαινα*) from its resemblance to black-lead), and also as a *plumbic molybdate* ($PbMoO_4$).

Preparation.—The sulphide is first roasted, whereby MoO_3 (molybdic anhydride) is formed. This is reduced by heating with charcoal.

Properties.—A white brittle metal, fusible with difficulty. It is oxidized by boiling with nitric acid. By heat it combines with chlorine ($MoCl_4$), forming red vapors, which condense to black scales.

It forms three oxides, viz., $Mo''O$, $Mo^{iv}O_2$, and $Mo^{vi}O_3$. MoO_3, which is known as molybdic anhydride, is prepared by roasting the sulphide and acting on the residue with ammonia, whereby molybdate of ammonia is formed, a salt largely used in the laboratory as a test reagent for the presence of phosphates, forming with phosphoric acid a phospho-molybdate of ammonia. At a red heat, molybdic anhydride fuses to a yellow glass, and sublimes. No definite hydrate is known.

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Molybdenum forms three sulphides, viz., MoS_2, MoS_3 (sulphomolybdic acid), and MoS_4 (persulphomolybdic acid).

It forms three chlorides, viz., molybdous chloride ($MoCl_2$), a sesquichloride (Mo_2Cl_6), and a molybdic chloride ($MoCl_4$).

Compounds of Molybdenum.

	SALTS.	Formula (General).	Formula (Constitutional).	Molecular Weight.
Oxides.	Molybdous oxide (protoxide)	MoO	$Mo''O$	112
	Molybdic oxide (dioxide)	MoO_2	$Mo^{iv}O_2$	128
	,, anhydride (trioxide)	MoO_3	$Mo^{vi}O_3$	144
Chlorides.	Molybdous chloride	$MoCl_2$	$Mo''Cl_2$	167
	Sesquichloride of molybdenum	Mo_2Cl_6	$'Mo'''Cl_3$ $'Mo'''Cl_3$	405
	Molybdic chloride (tetrachloride)	$MoCl_4$	$Mo^{iv}Cl_4$	238
Sulphides.	Molybdic disulphide	MoS_2	$Mo^{iv}S_2$	160
	,, trisulphide (sulpho-molybdic acid)	MoS_3	$Mo^{vi}S_3$	192
	Molybdic tetrasulphide (persulphomolybdic acid)	MoS_4	MoS_4	

Tests for Molybdenum Compounds.

(A.) Tests for *molybdous salts* (corresponding to $Mo''O$); *color*, black and opaque.

(B.) Tests for *molybdic salts* (corresponding to $Mo^{iv}O_2$); *color*, reddish brown.

(1.) *Sulphuretted hydrogen;* a brown ppt., soluble in ammonic sulphide.

(2.) *Sodic and potassic hydrates and their carbonates;* a brown ppt., soluble in ammonic carbonates.

(C.) Tests for *molybdates.*

(1.) A piece of zinc in a dilute acid solution of a molybdate, turns the liquid first blue, then green, then black.

(2.) *Stannous chloride;* a blue ppt. (MoO_2,$4MoO_3$).

(3.) *Acids;* a ppt. of MoO_3, soluble in excess.

All molybdenum compounds color a borax bead dark brown in the inner flame, and yellow in the outer flame. The color of the bead disappears on cooling.

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CHAPTER XVII.

THE METALS OF GROUP I.

LEAD and its Compounds—SILVER and its Compounds—MERCURY and its Compounds—THALLIUM and its Compounds—TUNGSTEN and its Compounds.

LEAD (Pb=207).

Atomic weight, 207. *Specific gravity*, 11·445. *Fuses*, 617° F. (325° C.). *Atomicity; dyad* ($PbCl_2$), *and tetrad* (PbO_2; $Pb(C_2H_5)_4$). *Sometimes a pseudo-triad.*

History.—The metal was known to the ancients (♄=scythe of Saturn).

Natural History.—It is not found native, but occurs almost entirely as a *sulphide*, "galena" (PbS). In small quantities it is found as a *carbonate* "white lead ore" ($PbCO_3$), and as a *sulphate*, "Anglesite" ($PbSO_4$).

Preparation.—*From Galena*—1. (*a.*) The ore is first of all mixed with a little lime, and then roasted with free access of air, in a reverberatory furnace. The following changes take place:—A part of the PbS becomes oxidized to $PbSO_4$; a second part loses its S (as SO_2), whereby PbO is left, whilst a third part remains undecomposed. Thus a mixture results of $PbSO_4$,PbS and PbO.

(*β.*) After the mixture of $PbSO_4$,PbO and PbS has been well incorporated, air is excluded, and the heat of the furnace raised. The following changes occur:—The sulphate and the oxide respectively decompose the lead sulphide, the metal being reduced, and SO_2 set free. Thus—

(*α.*)	$PbSO_4$	+	PbS	=	2Pb +	$2SO_2$.
	Lead sulphate	+	Lead sulphide	=	Lead +	Sulphurous anhydride.
(*β.*)	2PbO	+	PbS	=	3Pb +	SO_2.
	Lead oxide	+	Lead sulphide	=	Lead +	Sulphurous anhydride.

2. *Preparation of pure lead.*—The pure nitrate is ignited, and the oxide formed reduced with black flux.

Impurities.—Antimony (forming "*hard lead*"), manganese, silver, tin, iron, copper.

Purification ("*Refining. Improving*").—The lead is first melted. The tin and antimony present (which render the lead hard) oxidize more rapidly than the lead. The oxides of these metals are removed from the surface of the melted metal as fast as they are formed, leaving the lead in a pure state.

Extraction of Silver.—(1.) *Concentration of the silver alloy by Pattinson's process.*—This process depends on the circumstance that the alloy

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of silver and lead is more fusible than pure lead. The lead containing the silver is melted, and then well stirred as it cools. A portion of lead, almost entirely free from silver, first solidifies and sinks to the bottom of the vessel in the form of crystalline grains. The silver remains dissolved in the liquid metal, which is then poured off from the solid portion.

(2.) The silver is now obtained from this concentrated argentiferous alloy by "*cupellation*," as follows:—The alloy is exposed to a high temperature in a free current of air, whereby litharge (PbO) is formed. This PbO, which fuses at a low temperature, is then separated from the silver, by merely allowing the melted litharge to run off, thereby leaving the silver in a state of comparative purity.

Properties.—(α.) *Physical.* Lead is a bluish-white metal, very soft when pure. Its softness is more or less destroyed by the presence of plumbic oxide, a small quantity of which is soluble in the melted metal. It is not very malleable or ductile. By slow cooling it may be obtained in cubes and octahedra. At a heat of 617° F. (325° C.) it fuses, and at a white heat boils and volatilizes. It contracts considerably at the moment of solidification. It is inferior to most metals as a conductor of heat and electricity.

(β.) *Chemical. Action of air.*—A perfectly dry air is without action on lead at ordinary temperatures, but it rapidly tarnishes in moist air, a film of oxide forming on the surface of the lead, which prevents any further action. At high temperatures, the metal rapidly absorbs oxygen, emitting white fumes of lead oxide, and at the same time volatilizing slightly.

Action of water.—Pure un-aerated water has no action on lead.

Action of air and water.—Lead rapidly oxidizes from the combined influence of air and water, the water dissolving the lead oxide formed by the action of the air, leaving a clean surface of lead for the further action of the air. This solution of the oxide absorbs carbonic anhydride from the air, whereby a basic lead carbonate is precipitated ($PbCO_3$,PbH_2O_2). The water is then capable of dissolving fresh oxide as soon as it is formed on the surface of the lead. Thus the almost complete corrosion of metallic lead (as in *e. g.*, in old leaden coffins) is effected, with the conversion of the metal into a basic carbonate.

The *circumstances influencing this combined action of air and water on lead* are important, viz.:—

1. The presence of chlorides, nitrates, nitrites, and ammonia in the water *promote* corrosion.

2. The presence of sulphates, phosphates and carbonates, especially of calcic carbonate in water containing CO_2, *hinder* corrosion. The presence of *a limited quantity* of carbonic acid in water interferes with corrosion, by fixing on the lead a film of insoluble plumbic carbonate; whilst *an excess* of CO_2 may increase corrosion, plumbic carbonate being soluble in water highly charged with the gas. On

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boiling, the soluble lead carbonate subsides as the gas escapes. The presence of vegetable matter in water also hinders corrosion, by coating the metal with a compound of lead oxide and organic matter. In contact with air and sea-water an oxide and a chloride of lead are formed. Calcic sulphate, in the presence of moisture, rapidly corrodes lead. This is seen when lead pipes are placed in contact with plaster.

Action of Acids.—Sulphuric acid and hydrochloric acid do not act on lead at ordinary temperatures, and only slightly even when boiling. Nitric acid (especially if dilute) dissolves it, nitric oxide being liberated. Acetic acid dissolves it rapidly, changing it, in the presence of carbonic acid, to white lead. Hence green oak wood (which contains acetic acid) should never be placed near lead fittings in buildings, nor should metallic lead ever be allowed to be in contact with acid liquids that are used as food.

Salts of Lead.

		SALT.	Formula (Common).	Formula (Constitutional).	Molecular Weight.	Specific Gravity.	PbO or Pb per cent.
1.	Oxides.	Plumbous oxide; sub-oxide of lead ..	Pb_2O	$\left\{\begin{matrix}Pb\\Pb\end{matrix}\right\}O$			
2.	Oxides.	Plumbic oxide—(Litharge)	PbO	PbO	223	9·4	Pb=92·8
3.	Oxides.	Plumbic dioxide or peroxide (Plattnerite)	PbO_2	PbO_2	239	9·4	Pb=86·61
4.	Oxides.	*Minium* or *red leads*..	PbO,PbO_2 $2PbO,PbO_2$ $3PbO,PbO_2$	PbPbo″ Pb_2O_3″			
5.	Chlorides.	Plumbic chloride ..	$PbCl_2$	$PbCl_2$	278	5·8	Pb=74·46
6.	Chlorides.	Oxy-chlorides: Matlockite (Pattinson's white oxy-chloride).	$PbO,PbCl_2$	PbCl O PbCl			
	Chlorides.	Oxy-chlorides: Mendipite ..	$2PbO,PbCl_2$	PbCl O Pb″ O PbCl			
	Chlorides.	Oxy-chlorides: Patent or Turner's yelllow.	$7PbO,PbCl_2$	$Pb_8O_7Cl_2$			
7.	Chlorides.	Plumbic bromide ..	$PbBr_2$	$PbBr_2$	367	6·63	
8.	Chlorides.	Plumbic iodide	PbI_2	PbI_2	461	6·38	
9.	Chlorides.	Plumbic fluoride ..	PbF_2	PbF_2			
10.	Sulphides.	Plumbous sulphide ..	Pb_2S	$\left\{\begin{matrix}Pb\\Pb\end{matrix}\right\}S$			
11.	Sulphides.	Plumbic sulphide (galena)	PbS	PbS″	239	7·59	Pb=86·61
12.	Sulphides.	Plumbic persulphide..	PbS_5 (?)				
13.	Sulphides.	Plumbic selenide ..	PbSe			8·0	
14.	Sulphides.	Plumbic sulphate ..	$PbSO_4$	SO_2Pbo''	303	6·3	PbO=73·6
15.	Sulphides.	Plumbic nitrate.. ..	$Pb2NO_3$		331	4·4	PbO=67·37
16.	Sulphides.	Plumbic carbonate (lead spar)	$PbCO_3$	COPbo″		6·46	

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Alkalies have no special action on lead.

Chlorine acts on lead until a sufficient protective covering of lead chloride has been formed.

Uses.—For such alloys as type-metal (Pb and Sb), shot, solder, etc. The metal is largely used in building operations, as, *e.g.*, for cisterns, roofing, etc., and also in the construction of sulphuric acid chambers.

COMPOUNDS OF LEAD AND OXYGEN.

Plumbous oxide	Pb_2O.
Plumbic oxide	PbO.
Plumbic peroxide	PbO_2.
Red leads	Pb_2O_3; Pb_3O_4; Pb_4O_5.

(1.) Plumbous Oxide.—*Suboxide of lead* (Pb_2O).

Preparation.—(1.) By heating plumbic oxide to redness.

(2.) By heating lead oxalate to 608° F. (320° C.).

Properties.—A grey substance. Plumbic oxide and the metal are formed when plumbous oxide is acted upon by acids.

(2.) Plumbic Oxide.—*Lead protoxide* or *monoxide; litharge; massicot* (PbO).

Atomic weight, 223. *Specific gravity*, 9·5.

Preparation.—(1.) (*As a hydrate*, $2PbO,H_2O$; $3PbO,H_2O$). By precipitating lead solutions with alkalies.

(2.) (*Anhydrous*). By heating lead in air.

(3.) By igniting the carbonate.

Properties.—(α.) *Physical.* Lead oxide is found of various colors. It is *yellow*, if the heat used in its preparation be below that necessary to fuse the oxide (massicot); whilst it is *red* (due to Pb_2O_3) if the heat used be great (litharge). Litharge, when heated, turns brown, the brown color disappearing as the oxide cools. It fuses at a bright red heat, at which temperature it combines with silica and clay (such as clay crucibles) to form a fusible silicate of lead. It is easily reduced when heated with organic matter.

(β.) *Chemical.*—Litharge is slightly soluble in water, solution being *favored* by the presence of organic matter, and *hindered* by the presence of saline matters in the water. The solution is alkaline. It absorbs CO_2 from the air with great rapidity, a lead carbonate being precipitated. It is a powerful base, and exhibits a great tendency to form basic salts.

It is soluble in alkaline solutions, forming, with the alkalies, compounds that are easily decomposed.

Uses.—As a glaze for earthenware. Also in the manufacture of glass, on account of the ease with which it combines with silica at a high temperature. As a flux. For "dhil mastic" (a mixture of lead oxide and brickdust, made into a paste with linseed oil), a compound which sets very hard, and is used for repairing stone. As a hair dye

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(a solution of the oxide in lime-water), the sulphur of the hair forming the black PbS with the lead.

(3.) **Plumbic Peroxide** or *Dioxide.—Puce,* or *brown lead oxide* (PbO_2) [*Mol. Wt.* 239; *Sp. Gr.* 9·4]. This compound is found native (heavy lead ore).

Preparation.—(1.) By digesting red lead in boiling dilute nitric acid.

(2.) By fusing together litharge, potassic chlorate and nitre.

Properties.—A brown substance, insoluble in water and in acids. It is decomposed at a red heat ($2PbO_2=2PbO+O_2$). It acts as a powerful oxidising agent; hence its use in the manufacture of lucifer matches, for the purpose of igniting the sulphur, and in the laboratory as an absorbent of sulphurous anhydride ($PbO_2+SO_2=PbSO_4$). It forms, with hydrochloric acid, lead chloride, and with sulphuric acid, lead sulphate, chlorine being evolved in the former case, and oxygen in the latter. Its properties are acid rather than basic; hence it has been called *plumbic acid.* Thus it combines with the alkalies, as in the salt potassic plumbate ($K_2O,PbO_2,3H_2O$).

(4.) **Red Leads.**—*Minium.* A substance usually represented by the formula Pb_3O_4, and less frequently as Pb_2O_3 and Pb_4O_5.

Preparation.—By exposing plumbic oxide which has not been fused (massicot), to a faint red heat of 608° F. (320° C.), for some hours in the presence of air.

Properties.—A heavy red powder (Sp. Gr. 9·08), evolving oxygen when heated ($2Pb_3O_4=6PbO+O_2$). Most acids decompose it, forming plumbic salts and plumbic peroxide.

Uses.—In the manufacture of flint glass. For this purpose it must be very pure, for if other oxides be present, the glass will be colored.

(5.) **Plumbic Chloride** ($PbCl_2$) [*Mol. Wt.* 278; *Sp. Gr.* 5·8] is found native as "horn-lead."

Preparation.—By precipitating plumbic nitrate with hydrochloric acid.

Properties.—A white substance, almost insoluble in cold water, but soluble in boiling water (1 in 33), from which solution it is deposited in white needle-crystals on cooling. It fuses by heat into a horny substance, which at a higher temperature volatilizes.

(6.) There are several **Oxychlorides** of lead; *e.g.,* (1.) **Pattinson's white oxychloride** ($PbO,PbCl_2$), a compound used as a substitute for white lead. It is prepared by adding lime-water to a solution of $PbCl_2$ in hot water ($2PbCl_2+CaO=PbO,PbCl_2+CaCl_2$). (2.) **Mendipite** ($2PbO,PbCl_2$). (3.) **Turner's yellow** (Paris, patent or mineral yellow) ($7PbO,PbCl_2$), prepared by heating together litharge and ammonic chloride.

A red **Chlorosulphide of Lead** ($3SbS,2PbCl_2$) may be formed by precipitating an acid solution of plumbic chloride with H_2S, avoiding an excess of the gas.

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(8.) Plumbic Iodide (PbI_2) [*Mol. Wt.* 461 ; *Sp. Gr.* 6·38].

Preparation.—By mixing together solutions of plumbic acetate and potassic iodide.

Properties.—A bright yellow powder, soluble in hot water, the solution on cooling depositing golden scales.

A blue compound of an oxy-iodide with a lead carbonate is known ($Pb_2OI_4,4PbCO_3$).

COMPOUNDS OF LEAD AND SULPHUR.

1. Plumbous sulphide ... ... Pb_2S.
2. Plumbic sulphide ... ... PbS.
3. Plumbic persulphide ... ... PbS_5 (?).

(10.) Plumbous Sulphide.—*Subsulphide of lead* (Pb_2S). This body is produced during the process of smelting galena. It may be prepared by heating PbS in close vessels, part of the sulphur being expelled.

(11.) Plumbic Sulphide.—*Protosulphide of lead; galena* (PbS) [*Mol. Wt.* 239 ; *Sp. Gr.* 7·59]. Found native as galena.

Preparation.—(1.) (*As a hydrate.*) By the action of H_2S on a salt of lead.

(2.) (*Anhydrous.*) By fusing together sulphur and lead.

Properties.—When heated in air, a mixture of plumbic oxide and plumbic sulphate is formed, a part of the sulphur being expelled. Nitric acid converts it into a sulphate: boiling hydrochloric acid decomposes it, with the evolution of H_2S.

Lead Oxy-salts.

(15.) Plumbic Nitrate ($Pb2NO_3$). (*Mol. Wt.*, 331 ; *Sp. Gr.*, 4·4).

Preparation.—By dissolving the metal, or the oxide, or the carbonate of the metal, in dilute nitric acid.

Properties.—A white, opaque, crystalline (octahedral) substance, soluble in water (1 in 8 at 60° F.), and decomposed by heat into PbO, O, and N_2O_4.

Several *basic plumbic nitrates*, such as ($Pb2NO_3,PbH_2O_2$), etc., and also several *plumbic nitrites*, are known.

Lead combines with the various modifications of *phosphoric acid*, to form insoluble *plumbic phosphates* (*see* page 137).

Plumbic chromate ($PbCrO_4$) is a pigment known as chrome yellow.

(14.) Plumbic Sulphate ($PbSO_4$), (*Mol. Wt.*, 303 ; *Sp. Gr.*, 6·3), is found native as "Anglesite," or "lead vitriol," and also mixed with lead carbonate as "Lanarkite."

Preparation.—(1.) By adding sulphuric acid, or a soluble sulphate, to a salt of lead in solution.

(2.) It occurs as a secondary product in the manufacture of aluminic acetate.

Properties.—A white powder, soluble in ammonic acetate and in

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concentrated sulphuric acid, slightly soluble in nitric and in hydrochloric acids, insoluble in water.

A *plumbic sulphite* ($PbSO_3$) is known.

(16.) Carbonate of Lead ($PbCO_3$), (Sp. Gr. 6·46), is found native as "cerusite." *White lead*, or *ceruse*, is a basic carbonate (either $3PbCO_3,PbH_2O_2$ or $2PbCO_3,PbH_2O_2$).

Preparation of White lead.—The principal reactions involved in its preparation are as follows:—

(1.) The formation of *acetate of lead*, $Pb(C_2H_3O_2)_2$, by the action of acetic acid on oxide of lead.

(2.) *Tribasic acetate of lead* is then formed $[Pb(C_2H_3O_2)_2,2PbO]$, by combining the acetate of lead with two molecules of PbO.

(3.) By acting on this tribasic lead acetate with CO_2, the lead oxide is converted into carbonate, whilst the acetate of lead that remains is again capable of combining with more oxide. Thus—

$Pb(C_2H_3O_2)_2,2PbO$	+	$2CO_2$	=	$2PbCO_3$	+	$Pb(C_2H_3O_2)_2$.
Basic acetate of lead	+	Carbonic anhydride	=	Plumbic carbonate	+	Plumbic acetate.

Processes adopted in the Preparation of White Lead:—

(A.) *Dutch Process.*—A piece of lead is placed in an earthen pot containing crude vinegar. A large number of these pots, built up in heaps, are imbedded in spent tan, an arrangement being made by gratings for the supply of air. After some weeks, the lead becomes almost entirely converted into carbonate, the lead acetate combining with fresh plumbic oxide, as soon as that with which it is already combined is converted into carbonate. The vinegar supplies the acetic acid, and the putrifying organic matter (the tan) the carbonic anhydride. The carbonate is then ground and levigated, an operation which acts very deleteriously on the work-people.

(B.) *Thénard's Process.*—This consists in boiling together litharge and acetic acid, and decomposing the tribasic acetate formed, with a current of carbonic anhydride. The product is said to be inferior as a pigment to that prepared by the former process.

Properties.—Lead carbonate is insoluble in water, unless the water be charged with carbonic acid. Heat decomposes it into CO_2 and PbO. Acids dissolve it, with effervescence.

In common with all lead salts, lead carbonate is blackened by a mere trace of sulphuretted hydrogen. The blackening, however, disappears on prolonged exposure to light and air, the black plumbic sulphide becoming converted into the white plumbic sulphate.

Reactions of Lead Compounds.—(*See* ANALYTICAL TABLES.)

SILVER (*Argentum*) (Ag′=108).

Atomic weight, 108. *Molecular weight* (*probable*), 216. *Specific gravity*, 10·5. *Fuses at* 1681° F. (916° C.). *Atomicity monad.* ($AgCl$; Ag_2O.)

History.—Silver was known to the ancients (☽ = Luna).

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Natural History.—Silver is found in a free state. It also occurs as a *sulphide*, "silver glance;" as a *chloride*, "horn silver;" and as a *carbonate*; also as a compound of *bromide* and *chloride*, "embolite" (2AgBr,3AgCl); and as a *sulphantimonite*, "dark-red silver ore." It is present in small quantities (2 or 3 ozs. per ton) in galena (PbS).

Extraction.—(1.) *Liquation Process of Pattinson.*—From argentiferous lead (*see* page 410).

(2.) *Amalgamation Process.*—The powdered ore is first roasted with sodic chloride, whereby a silver chloride is formed. The mass is then agitated in water, with mercury and scraps of iron. The iron reduces the silver to the metallic state, whilst the mercury dissolves the reduced silver. The amalgam is then heated, by which means the separation of the mercury from the silver is effected.

Preparation of pure Silver.—Dissolve the impure metal in nitric acid; precipitate the silver as AgCl, with hydrochloric acid; collect, wash, dry, and fuse the precipitated chloride with anhydrous sodic carbonate in an earthen crucible.

Properties.—(*a.*) *Physical.* A white metal, with high lustre, very malleable and ductile, and the best conductor of heat and electricity known. It may be crystallized. Specific gravity, 10·5. It is harder than gold, but not so hard as copper. Very thin leaves are said to transmit a bluish-green light.

It is slightly volatile by heat. It fuses at 1681° F. (916° C.), expanding greatly at the moment of its solidification.

(*β.*) *Chemical.* Silver is unaltered at any temperature either by moisture or by air (Ozone probably oxidizes it). When melted, however, in air, it mechanically absorbs more than 22 times its bulk of oxygen, disengaging it again as it solidifies. (This accounts for what is known as the *spitting* of the globule.) This absorption of oxygen may be prevented by the addition of 1 or 2 per cent. of copper to the silver.

Action of Acids.—Hot sulphuric and dilute nitric acids dissolve it. With the former, Ag_2SO_4 is formed, and SO_2 evolved; and with the latter, $AgNO_3$ is formed, and nitric oxide (N_2O_3) evolved. Hydrochloric acid is decomposed by the red hot metal, hydrogen and argentic chloride being formed.

Silver is unaffected by the alkalies. It combines with the haloids. If NaCl be fused, or even kept for a time in a silver dish, AgCl and NaHO will be formed. It unites when fused with phosphorus. Its attraction for sulphur is great; hence, when exposed to the air it rapidly blackens, Ag_2S being formed by the action upon it of the H_2S present in the atmosphere.

Uses.—For coinage and plate (925Ag and 75Cu = 1000 English standard silver). "Frosted silver" is produced by heating the silver in air and immersing it when hot in dilute sulphuric acid. *Oxidized silver* is produced by dipping the metal in a solution obtained by

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boiling together sulphur and potash, whereby the silver becomes covered with a minute film of sulphide. Electro-plating is performed by depositing silver on some baser metal by electrical agency.

Compounds of Silver.

	SALTS.	Formula (Common).	Formula (Constitutional).	Molecular Weight.	Specific Gravity.	Ag or Ag_2O per cent.
1.	Oxides. Argentous oxide	Ag_4O (?)	OAg_4 (?)			
2.	Argentic oxide	Ag_2O	OAg_2	232·0	7·2	Ag=93·1
3.	,, peroxide ..	Ag_2O_2	$\begin{cases} OAg \\ OAg \end{cases}$	248·0	5·47	
4.	Chlorides. Argentous chloride ..	Ag_2Cl (?)	Ag_2Cl (?)			
5.	Argentic chloride.. ..	AgCl	AgCl	143·5	5·55	Ag=75·26
6.	,, bromide.. ..	AgBr	AgBr	188·0	6·35	Ag=57·45
7.	,, iodide	AgI	AgI	235·0	5·5	Ag=45·96
8.	,, fluoride	AgF	AgF	127·0		
9.	,, sulphide.. ..	Ag_2S	Ag_2S	248·0	7·2	Ag=87·1
10.	,, sulphate ..	Ag_2SO_4	SO_2Ago_2	312·0	5·32	Ag_2O=74·36
11.	,, nitrate	$AgNO_3$	NO_2Ago	170·0	4·33	Ag_2O=68·24
12.	,, carbonate ..	Ag_2CO_3	$COAgo_2$			
13.	Triargentic phosphate..	Ag_3PO_4	$POAgo_3$	419·0	7·32	
14.	Argentic pyrophosphate	$Ag_4P_2O_7$	$P_2O_3Ago_4$		5·30	
15.	,, metaphosphate	$AgPO_3$	PO_2Ago			
16.	,, hyposulphate..	$Ag_2S_2O_6$(?)				
17.	,, thiosulphate ..	$Ag_2S_2O_3$	$SS''OAgo''$			

Compounds of Silver and Oxygen.

Argentous oxide	Ag_4O.
Argentic oxide	Ag_2O.
Argentic peroxide	Ag_2O_2.

(1.) Argentous Oxide; *Suboxide of silver* (Ag_4O).

Preparation.—By heating argentic citrate to 212° F. (100° C.) in a stream of hydrogen. The residue, which contains argentous citrate, is then dissolved in water, and the argentous oxide precipitated from the solution by potassic hydrate.

Properties.—A black powder, easily decomposed by heat and by chemical reagents. It is soluble in ammonia.

(2.) Argentic Oxide; *Protoxide of silver* (Ag_2O). [*At. Wt.*, 232; *Sp. Gr.*, 7·2].

Preparation.—By the action of a heat of 140° F. (60° C.) on the brown hydrated oxide, produced when potassic hydrate is added to a solution of a soluble silver salt.

Properties.—(*a.*) *Physical.* A brown substance, decomposed at a red heat ($Ag_2O=Ag_2+O$), and also partially by the action of sunlight.

(*β.*) *Chemical.*—Argentic oxide is a powerful base, completely neutralizing acids, the salts formed being isomorphous with the

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alkaline salts. Its solution in water (in which it is slightly soluble) is feebly alkaline. It is insoluble in solutions of sodic or of potassic hydrates, but dissolves readily in ammonia, the solution slowly depositing the explosive argentic nitride, or "*fulminating silver*" (Ag_3N?). It forms a yellow glass with the fusible silicates.

(3.) **Argentic Peroxide** (Ag_2O_2) is deposited in small grey crystals on the positive pole of the battery, when a voltaic current is passed through a solution of argentic nitrate. With nitric and sulphuric acids, oxygen is liberated, and argentic salts formed. From hydrochloric acid it liberates chlorine. It both decomposes and is decomposed by ammonia, nitrogen being evolved.

COMPOUNDS OF SILVER AND CHLORINE.

Argentous Chloride	...	...	...	Ag_2Cl.
Argentic Chloride ...	...	...	...	$AgCl$.

(4.) **Argentous Chloride**, *Subchloride of silver* (Ag_2Cl).

Preparation.—Either by precipitating a solution of argentous citrate with sodic chloride, or by the action of ferric chloride on metallic silver ($2Ag_2 + Fe_2Cl_6 = 2Ag_2Cl + 2FeCl_2$).

Properties.—A black substance insoluble in nitric acid. By the action of heat or of an ammonia solution, it is converted into silver and argentic chloride.

(5.) **Argentic Chloride** ($AgCl$).—[*Mol. Wt.* 143·5; *Sp. Gr.* 5·5]. Silver chloride is found native both in cubical crystals, and also as a compact semi-transparent mass called "horn silver." It is found associated with argentic bromide in "embolite."

Preparation.—By adding hydrochloric acid, or a soluble chloride, to a soluble silver salt.

Properties.—A white substance becoming violet on exposure to light, Ag_2Cl and free chlorine being formed. The decomposition is less rapid if the chloride be very pure, and more rapid if organic matter be present. It melts at 500° F. (260° C.) becoming a horny mass as it cools. It is slightly volatile, but does not decompose at a high temperature. It is insoluble in nitric acid, but is soluble in boiling concentrated hydrochloric acid (1 in 200) from which solution it may be precipitated by dilution with water. It is also soluble in solutions of the alkaline and earthy chlorides, forming with them double salts. Ammonia dissolves it freely, depositing crystals of the chloride on evaporation. Cold solutions of potassic or sodic hydrates do not act upon it, but when concentrated alkaline solutions are boiled with argentic chloride, an alkaline chloride is formed, and argentic oxide precipitated. The oxide is reduced when heated with glucose. The chloride absorbs ammonia gas freely, but gives it up when heated. It is soluble in solutions of the hyposulphites (thiosulphates), also in the soluble sulphites and in potassic cyanide. When digested in

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solutions of potassic bromide or iodide, argentic bromide and iodide are formed, potassic chloride remaining in solution. It is not reduced when heated with carbon; but it is reduced either:—(1.) When heated in a current of hydrogen ($2AgCl+H_2=Ag_2+2HCl$); or, (2.) When ignited with the alkaline carbonates ($4AgCl+2Na_2CO_3=4NaCl+2CO_2+O_2+2Ag_2$); or, (3.) When brought into contact with the easily oxidisable metals (*e.g.*, Zn, Fe, &c.). The chloride is largely used in photography.

(6 and 7.) Argentic Bromide ($AgBr=188$) and **Argentic Iodide** ($AgI=235$).

Preparation.—By adding potassic bromide or potassic iodide, to a solution of argentic nitrate.

Properties.—Both salts have a yellow colour. They are insoluble in acids, not very soluble in ammonia, but freely soluble in a solution of sodic hyposulphite (thiosulphate).

Argentic iodide is soluble in a boiling solution of argentic nitrate, crystals being deposited on cooling, having the formula ($AgI,AgNO_3$). These crystals are more sensitive to light even than the iodide.

Compounds of Silver and Sulphur.

(9.) Argentic Sulphide (Ag_2S). [*Mol. Wt.* 248; *Sp. Gr.* 7·2.]

Natural History.—It is found native, both massive and in crystals, as "silver glance." It also occurs combined with the sulphides of antimony and arsenic as "dark" and "light-red silver ores."

Preparation.—(1.) By passing sulphuretted hydrogen through a solution of a salt of silver.

(2.) By heating the metal with sulphur in a covered crucible.

Properties.—(a.) *Physical.* It is a soft, dark-coloured, fusible body, conducting electricity when hot, but not when cold. It fuses when heated, if air be excluded, but is decomposed when roasted in the open air.

Boiling sulphuric acid forms with it argentic sulphate and SO_2. Boiling hydrochloric acid forms argentic chloride and H_2S. Nitric acid forms with it a yellow body, having the formula ($Ag_2S,AgNO_3$). The alkalies decompose it, when heated with it. It is not soluble in the alkaline sulphides. It is decomposed by cupric chloride, argentic chloride being formed, and also by ignition with many of the metals, such as Cu, Pb, Fe, etc.

Oxy-Salts of Silver.

(10.) Argentic Sulphate (Ag_2SO_4). [*Mol. Wt.* 312; *Sp. Gr.* 5·32.]

Preparation.—By boiling together silver and sulphuric acid, from which solution the salt may be precipitated on the addition of water.

Properties.—A crystalline body, somewhat insoluble in water (1 in 200 aq. at 60° F.; 1 in 88 aq. at 212° F.).

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An acid sulphate ($AgHSO_4$) has also been prepared.

(11.) Argentic Nitrate.—*Nitrate of silver; lunar caustic* ($AgNO_3$). [*Mol. Wt.*, 170; *Sp. Gr.*, 4·33; fuses at 426° F. (219° C.)]

Preparation.—By dissolving the metal in nitric acid, and crystallising or evaporating the solution to dryness.

Properties.—A colorless crystalline salt, unacted upon by light if perfectly pure, but blackened in the presence of a trace of organic matter. It is soluble in water (1 in 1 at 60° F.; 2 in 1 at 212° F.), and also in boiling alcohol (1 in 4), but is insoluble in nitric acid. It fuses at 426° F. (219° C.), and, when cast into sticks, forms what is called "lunar caustic." At a higher temperature it decomposes.

It is used in surgery as an escharotic. This action depends on the readiness with which it parts with its oxygen, the oxygen combining with the organic matter and the silver being precipitated. It is used in photography, also in hair-dyes, and for marking inks. In the case of marking inks, either the fabric is first mordanted with sodic carbonate, and then written upon with an argentic nitrate solution, whereby an argentic carbonate is precipitated—a salt easily blackened; or else the fabric is written upon without preparation with a solution of argentic nitrate, containing an excess of ammonia, which combines with the nitric acid of the silver-salt.

MERCURY. Quicksilver (Hg=200).

Atomic and molecular weight, 200. *Molecular and atomic volume*, [|]. *Specific gravity at* 60° F. (15·5° C.) 13·56; *of vapor*, 6·97°. *Fuses at* 37·9° F. (38·8° C.). *Boils at* 675° F. (35·7° C.). *Atomicity, dyad in mercuric compounds* ($HgCl_2$); *also a pseudo-monad, as in mercurous compounds* (Hg_2Cl_2).

History.—Known to the ancients.

Natural History.—It occurs native, but is found chiefly as *a sulphide*, "Cinnabar" (HgS). It is also found as a *chloride* (Hg_2Cl_2), and as an *iodide*.

Extraction.—(1.) *Process at Almaden.* The ore (HgS) is roasted, and the mercury condensed as it distils over. The sulphurous acid is allowed to escape.

(2.) *Process in the Palatinate.*—The ore (HgS) is distilled with lime. The mercury passes over and is collected, whilst the sulphur remains in the retort as calcic sulphide and sulphate ($4HgS+4CaO=3CaS+CaSO_4+2Hg_2$). (Scraps of iron may be used instead of lime, when ferrous sulphide remains in the retort.)

Impurities.—Chiefly tin and lead.

Properties.—(α.) *Physical.* Mercury is a silvery-white, lustrous, liquid metal. It is the only liquid metal known. It becomes solid at

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— 37·9° F. (— 38·8° C.), contracting greatly as it solidifies. The solid mercury has a specific gravity of 14·0. It crystallizes in octahedra, and is very malleable. Above 41° F. (5° C.) mercury is slightly volatile. The vapor (Sp. Gr., 6·97) is transparent, and neither conducts heat nor electricity. At 675° F. (357° C.) the metal boils.

[NOTE.—The vapor density of mercury compared to air is 6·7, and to hydrogen 100;—that is, its vapor density is one-half its atomic weight; hence the mercury atom (like the cadmium atom) occupies as a gas, twice the volume occupied by the hydrogen atom.]

(β.) *Chemical.* It is not tarnished (if pure) either by air or water at ordinary temperatures, although it appears that, when reduced to a minute state of subdivision, as, *e.g.*, by trituration with various substances chemically inert upon it, as in the preparation of the Hyd. c. cret., and pil. hydrargyri, etc., of the Pharmacopœia, it undergoes a partial oxidation (Hg_2O), to which the active properties of these medicines are probably due. It rapidly absorbs oxygen when heated to 800° F. (426° C.), becoming the red oxide of mercury (HgO). At a dull red heat this oxide is decomposed into mercury and oxygen. It combines at common temperatures with sulphur, with the haloids, and also with many of the metals, forming with them definite compounds. Iron and platinum are the only metals not corroded by mercury.

Neither hot nor cold hydrochloric acid, nor cold sulphuric acid have any action upon it. With hot sulphuric acid, mercury forms a sulphate, SO_2 being evolved. With strong nitric acid, a mercuric nitrate is formed, nitric oxide being evolved, whilst by the action of dilute nitric acid a mercurous nitrate results.

Uses.—In medicine, as blue pill, grey powder, etc. Its action on the body is intense. Workmen exposed to the action of mercury vapor, become affected with mercurial palsy. It is also used as an amalgam with tin, for silvering looking-glasses. Also for amalgamating zinc plates, and for the extraction of gold and silver from their ores, depending on the readiness with which it forms an amalgam with them.

COMPOUNDS OF MERCURY AND OXYGEN.

Mercurous oxide	...	...	...	Hg_2O.
Mercuric oxide	...	...	...	HgO.

(1.) **Mercurous Oxide.**—*Suboxide*, or *black*, or *grey oxide of mercury* (Hg_2O). [*Molecular weight*, 416. *Specific gravity*, 10·68.]

Preparation. — By decomposing calomel with potassic hydrate ($Hg_2Cl_2 + K_2O = Hg_2O + 2KCl$).

Properties.—A powerful base. It is decomposed by the slightest heat, or even by mere exposure to light ($2Hg_2O = 2HgO + Hg_2$).

The efficacy of blue pill, grey powder, etc., is believed to be due to the presence of this oxide.

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Compounds of Mercury.

	SALTS.	Formula (General).	Formula (Constitutional).	Molecular Weight.	Specific Gravity.	Hg per cent.
1. Chlorides. Oxides.	Mercurous oxide (black oxide)	Hg_2O	$'Hg'_2O$	416	10·68	Hg=96.15
2. Chlorides. Oxides.	Mercuric oxide (red oxide)	HgO	HgO	216	11·29	Hg=92·59
3. Chlorides. Oxides.	Mercurous chloride (calomel)	Hg_2Cl_2	$'Hg'_2Cl_2$	471	7·14	Hg=84·92
4. Chlorides. Oxides.	Mercuric chloride (corrosive sublimate)	$HgCl_2$	$HgCl_2$	271	5·42	Hg=73·80
	[Bromides analogous to chlorides].					
5.	Mercur-ammonic chloride (white precipitate)	$NH_2Hg''Cl$	$NH_2Hg''Cl$			
6.	Mercurous iodide (green)	Hg_2I_2	$'Hg'_2I_2$	654		
7.	Sesqui-iodide of mercury (yellow)	Hg_2I_3				
8.	Mercuric iodide (red)	HgI_2	HgI_2	454	6·25	Hg=44·05
9. Sulphides.	Mercurous sulphide (Ethiop's mineral)	Hg_2S	$'Hg'_2S''$			
10. Sulphides.	Mercuric sulphide (vermilion)	HgS''	HgS	232	8·2	Hg=86·21
11.	Mercurous sulphate	Hg_2SO_4	$SO_2('Hg'_2O_2)''$			
12.	Mercuric sulphate	$HgSO_4$	SO_2Hgo''	296	6·46	
13.	Trimercuric suphate (Turpeth mineral)	$HgSO_4,2HgO$	$SHgo''_3$		8·319	
14.	Mercurous nitrate or Tetrahydric mercurous dinitrate	$(Hg_2)''2NO_3,2H_2O$	$N_2O_2Ho_4('Hg'_2O_2)''$			
15.	Mercuric nitrate	$2Hg''2NO_3,H_2O$				

(2.) **Mercuric Oxide.**—*Nitric oxide*, or *Red oxide of mercury; Red precipitate* (HgO). [*Molecular weight*, 216. *Specific gravity*, 11·29.]

Preparation.—(1.) By heating mercury to 800° F. (426° C.) in air.

(2.) By gently calcining mercuric nitrate. Hence the name *nitric-oxide of mercury*. (These two varieties are red and crystalline.)

(3.) By mixing together solutions of sodic hydrate, and either mercuric chloride or mercuric nitrate. (This variety is amorphous, and of a yellow colour.)

Properties.—(α.) *Physical.* The oxide is black when hot, and either red and crystalline, or yellow and amorphous when cold. The yellow variety has the most marked chemical affinities. The oxide is decomposed at a dull red heat (HgO=Hg+O). It is slightly soluble in water, the solution having an alkaline reaction and a metallic taste.

(β.) *Chemical.* The red and yellow forms appear to be allotropic modifications of the same salt:—

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(1.) The *yellow* variety is converted, by a cold solution of oxalic acid, into an oxalate. It is rapidly changed into an oxychloride when boiled with a solution of mercuric chloride, and, when boiled with potassic bichromate, yields a basic mercuric chromate ($HgCrO_4,2HgO$).

(2.) The *red* variety, is not acted upon by oxalic acid. It is very slowly acted upon by a mercuric chloride solution, and when boiled with potassic bichromate, forms the compound $HgCrO_4,3HgO$.

It is soluble in fused potassic or sodic hydrate, from which solution a crystalline body may be obtained (K_2O,HgO).

By the action of ammonia upon mercuric oxide, the *ammoniated oxide of mercury* is formed ($4HgO,2NH_3,2H_2O=Hg_2H_5NO_3$). This compound is a yellowish substance, easily decomposed by friction, or even by exposure to light. Chemically, it possesses strong basic properties. When dried "in vacuo" over sulphuric acid, it loses $2H_2O$, and forms the compound $4HgO,2NH_3$. When this body is heated to 260° F. (126·1° C.), it becomes *mercuramine* ($Hg_4O_3N_2H_4$, or $\left.\begin{matrix}Hg_4N_2\\H_2\end{matrix}\right\}O_2,H_2O$, or $\left.\begin{matrix}H_2\\H_2\\Hg''\end{matrix}\right\}N_2,3HgO$), a dark brown substance, insoluble in water or in alcohol. It acts as a powerful base. It will be seen by the formulas given, that different views are entertained as to its constitution. Most chemists regard it as a compound of mercuric oxide and two ammonia molecules, where two atoms of hydrogen have been displaced by one of dyad mercury.

By passing ammonia gas over the yellow oxide, and then cautiously heating the residue to 260° F. (126·1° C.), a brown explosive *nitride of mercury* ($N_2Hg''_3$) is formed. By the action of acids this body yields salts of mercury and ammonium. It may be regarded as a double ammonia molecule, where six atoms of hydrogen are displaced by three atoms of divalent mercury.

COMPOUNDS OF MERCURY AND CHLORINE.

Mercurous chloride	Hg_2Cl_2.
Mercuric chloride	$HgCl_2$.
Mercur-ammonic chloride	$NH_2Hg''Cl$.

(3.) Mercurous Chloride.—*Subchloride* or *Protochloride of mercury; Calomel* (Hg_2Cl_2).

[*Molecular weight*, 471. *Specific gravity, solid*, 7·14; *of vapor*, 8·14. *Molecular volume, anomalous*, . *Relative weight*, 119·2.]

Preparation.—(1.) By precipitating a solution of mercurous nitrate with hydrochloric acid, or with sodic chloride.

(2.) By subliming a mixture of corrosive sublimate (17 parts) and mercury (13 parts) ($HgCl_2+Hg=Hg_2Cl_2$).

(3.) By well triturating together mercuric sulphate (2 parts), mer-

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cury (4 parts), sodic chloride (3 parts), and subsequently subliming the mixture ($HgSO_4 + Hg + 2NaCl = Hg_2Cl_2 + Na_2SO_4$).

(4.) By passing sulphurous anhydride through a saturated solution of crystalline mercuric chloride, heated to 122° F. (50° C.) ($2HgCl_2 + 2H_2O + SO_2 = Hg_2Cl_2 + 2HCl + H_2SO_4$).

Impurity.—Corrosive sublimate may be present, derived partly from the sublimation of undecomposed mercuric chloride, and partly from the decomposition of the calomel into mercury and mercuric chloride (dissociation). Its presence may be detected by heating a little of the calomel moistened with alcohol on a clean knife-blade, when a black spot will be formed if corrosive sublimate be present. The calomel may be purified by thorough washing with water.

Properties.—(*a.*) *Physical.* A white, heavy, tasteless, insoluble compound. It may exist both in an amorphous and crystalline (four-sided prisms) condition. It sublimes before fusing.

The experimental vapor density of calomel (hydrogen being 1) is 119·2. If we allow Hg_2Cl_2 to be the molecule of calomel, occupying 2 vols. as a gas, its theoretical density is nearly double its experimental density (*i.e.*, $\frac{400(2Hg)+71\ 2Cl)}{2} = 235{\cdot}5$). If we regard the molecule to be HgCl, then the actual and observed densities almost correspond. Why then do we not adopt HgCl as the formula for calomel? For two reasons:—(1.) Because it interferes with the theory that a dyad element (like Hg″) can unite with an *uneven* number of monad elements (like Cl′) (*see* page 39); and (2.) That when mercurous salts are decomposed, they invariably form mercuric salts, free mercury being produced, thus favoring the notion that the molecule of the mercurous salt contains 2 atoms of mercury rather than 1 atom. *Can we then explain this anomalous vapor density of calomel?* It is believed that at high temperatures the salt undergoes *dissociation* (*see* pages 13 and 47), the 2 volumes of mercurous chloride splitting up into 2 volumes of mercuric chloride and 2 volumes of mercury, making in all 4 volumes instead of 2 volumes. The vapor density of mercurous bromide is also similarly anomalous.

(*β.*) *Chemical.* Solutions of sodic and potassic hydrates or lime-water decompose it, forming mercurous oxide (Hg_2O), or black oxide of mercury ($Hg_2Cl_2 + CaO = Hg_2O + CaCl$) (a mixture known as "black wash.") With ammonia it forms the black compound Hg_2H_2NCl; ($Hg_2Cl_2 + 2H_3N = Hg_2H_2NCl + H_4NCl$). Sulphuric acid has no action upon it. Boiling nitric acid dissolves it, forming mercuric nitrate and chloride. Boiling hydrochloric acid, and solutions of sodic or ammonic chlorides also dissolve it, forming mercuric chloride, and precipitating the metal.

(4.) Mercuric Chloride; *Chloride, Bichloride* or *Perchloride of mercury; Corrosive Sublimate* ($HgCl_2$).

Molecular weight, 271. *Relative weight,* 135·5. *Specific Gravity of solid,* 5·42; *of vapor,* 9·8.

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Preparation. (1.) By heating together mercury and chlorine.

(2.) By subliming a mixture of mercuric sulphate and common salt ($HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2$).

Properties.—(α.) *Physical.* A white heavy crystalline (octahedral) substance, having an acrid metallic taste. It sublimes at a low temperature, fuses at 509° F. (265° C.), and boils at 563° F. (295° C.), the vapours evolved being condensible and very poisonous. It is freely soluble in water (1 in 16 at 60° F., 1 in 3 at 212° F.); in alcohol (1 in 3 at 60° F., 1 in 1 at 212° F.); in ether (1 in 3); and in solutions of the alkaline chlorides. Ether dissolves it from its aqueous solution. It is intensely poisonous. It is a powerful antiseptic.

(β.) *Chemical.* The aqueous solution is acid to litmus, and is decomposed by light with the precipitation of calomel. Alkalies decompose it. With ammonic chloride it forms a double salt called "sal alembroth" ($HgCl_2, 6NH_4Cl, H_2O$).

Mercuric Oxy-chlorides.—These are formed by the combination of mercuric chloride with mercuric oxide. Three of them (and indeed more) have been described, all being formed by the action of potassic carbonate on mercuric chloride, viz.:—

(1.) $2HgO, HgCl_2$. (2.) $3HgO, HgCl_2$. (3.) $4HgO, HgCl_2$.

No. 1 ($2HgO, HgCl_2$) is formed by adding a cold saturated solution of potassic hydric carbonate to eight or ten times its bulk of a cold saturated solution of mercuric chloride (red oxychloride).

No. 2 ($3HgO, HgCl_2$) is formed by mixing together equal volumes of the solutions (yellow oxychloride).

No. 3 ($4HgO, HgCl_2$) is formed by adding a mercuric chloride solution to a large excess of a hydric potassic carbonate solution.

We may here remark that if a mercuric chloride solution be added to *normal* sodic or potassic carbonate, a *yellow* mercuric oxide is precipitated; but that if it be added to *hydric* sodic or *hydric* potassic carbonate (bicarbonate), a *red oxychloride* is formed.

(5.) **Mercur-ammonic Chloride,** *White precipitate,* (*Mercurius precipitatus albus*) ($NH_2Hg''Cl$).

Preparation.—By adding a solution of corrosive sublimate to an excess of a solution of ammonia ($HgCl_2 + 2H_3N = NH_2Hg''Cl + NH_4Cl$).

Constitution.—The importance of this compound depends on the fact of its having been the first recorded case where the mobility of hydrogen was recognised. White precipitate (that is the precipitate formed where *the ammonia is in excess*) is regarded as ammonic chloride where the dyad Hg″ has replaced two atoms of the monad hydrogen. Thus—

NH_4Cl = *ammonic chloride,* and $NH_2Hg''Cl$ = *white precipitate.*

If *the mercuric chloride be in excess,* the body $N_2H_4Hg_4Cl_6$ is formed. This compound is regarded as a double molecule of ammonic chloride, in which 4 of the monad group $(HgCl)'$ has replaced 4 atoms of hydrogen. Thus—

$N_2H_8Cl_2$ = 2 of *ammonic chloride;* $N_2H_4(HgCl)'_4Cl_2$ = the *precipitate.*

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Properties.—When white precipitate is boiled with water a yellow powder is produced ($Hg_4N_2Cl_2,2H_2O$). Thus—

$$4Hg''H_2NCl + 2H_2O = Hg_4N_2Cl_2,2H_2O + 2H_4NCl.$$
White precipitate + Water = Yellow precipitate + Ammonic chloride.

Boiled with potassic hydrate, white precipitate forms NH_3 and HgO. Thus—

$$Hg''H_2NCl + KHO = NH_3 + HgO + KCl.$$
White precipitate + Potassic hydrate = Ammonia + Mercuric oxide + Potassic chloride.

Heated to 608° F. (320° C.) a red crystalline powder is formed ($2HgCl_2,Hg_3N_2$). Thus—

$$6Hg''H_2NCl = 3NH_3 + H_3N,HgCl_2 + 2HgCl_2,Hg_3N_2.$$
White precipitate = Ammonia + + Red powder.

Boiled with a solution of ammonic chloride "fusible white precipitate" is formed ($Hg''H_6N_2Cl_2$). Thus—

$$Hg''H_2NCl + NH_4Cl = Hg''H_6N_2Cl_2.$$
White precipitate + Ammonic chloride = Fusible white precipitate.

White precipitate is used as a poison for destroying vermin.

Compounds of Mercury and Iodine.

Mercurous iodide	Hg_2I_2.
Sesqui-iodide of mercury ...	$(HgI,HgI_2)=Hg_2I_3$.
Mercuric iodide	HgI_2.

(6.) Mercurous Iodide (Hg_2I_2).

Preparation.—By triturating 5 parts of iodine with 8 parts of mercury, the mixture being moistened with a little alcohol.

Properties.—A *green* insoluble powder, decomposed both by light and heat into mercuric iodide and metallic mercury.

(8.) Mercuric Iodide.—*Biniodide of mercury* (HgI_2).

[*Molecular weight*, 454. *Relative weight*, 227. *Specific gravity of solid*, 6·2·5; *of vapor*, 15·708.]

Preparation.—(1.) By triturating together 5 parts of iodine and 4 of mercury, and subliming the mixture.

(2.) By precipitating a solution of mercuric chloride with one of potassic iodide.

[The mercuric iodide is soluble in excess of either salt.]

Properties.—(*a.*) *Physical.* Mercuric iodide is dimorphous. If the crystals be octahedral, the color of the salt is red; if they be rhomboidal, it is yellow. It is soluble in hot alcohol, but is insoluble in water. It fuses at 392° F. (200° C.). The vapor has a remarkably high specific gravity (15·708).

(*β.*) *Chemical.* It is soluble in the alkaline chlorides, in neutral ammonic salts, and in hydrochloric and hydriodic acids. With the more basic, or electro-positive soluble metallic iodides, it forms double salts. Thus potassic-mercuric iodide ($2(KI,HgI_2),3H_2O$) crystallizes

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on cooling from a hot solution of mercuric iodide in potassic iodide. It forms double salts with mercuric oxide, sulphide, and chloride, as *e.g.* (HgI_2,$HgCl_2$) and (HgI_2,$2HgCl_2$).

The solution of mercuric iodide in a solution of potassic iodide containing potassic hydrate, constitutes the "Nessler test" for ammonia. This solution forms, with ammonia, a brown precipitate (Hg''_2NI,H_2O).

Reaction of the Nessler test with ammonia—

$$2HgI_2 + 3KHO + NH_3 = Hg''_2NI,H_2O + 3KI + 2H_2O.$$

COMPOUNDS OF MERCURY AND SULPHUR.

Mercurous sulphide	...	...	...	Hg_2S.
Mercuric sulphide	...	...	...	HgS.

(9.) **Mercurous Sulphide.** — *Subsulphide of mercury; Ethiop's mineral* (Hg_2S).

Preparation.—By passing sulphuretted hydrogen through a solution of mercurous nitrate.

Properties.—A black substance, easily decomposed by heat ($Hg_2S = Hg + HgS$).

(10.) **Mercuric Sulphide.**—*Cinnabar* (that is, the native HgS); *Vermilion* (that is, the finely-powdered HgS) (HgS).

[*Molecular weight*, 232. *Relative weight, anomalous*, 77·3, *i.e.*, 2 *volumes of mercury vapor* + 1 *volume of sulphur vapor forms* (*not* 2 *volumes but*) 3 *volumes of mercuric sulphide vapor; that is, they unite without condensation. Molecular volume,* [ ]. *Specific gravity of solid*, 8·2; *of vapor*, 5·5.]

Natural History.—It is found native both in crystals (hexahedra) and in masses. It constitutes the principal ore of mercury.

Preparation.—(1.) By adding a solution of mercuric chloride, either to a solution of sulphuretted hydrogen, or to one of a soluble sulphide (black variety of HgS).

(2.) By agitating together 6 parts of mercury and 1 of sulphur (black variety of HgS).

(3.) The red form of sulphide is prepared from the black, either by subliming the black variety in vessels from which air is excluded, or by the prolonged action of an alkaline sulphide containing an excess of sulphur.

(4.) By triturating 300 parts of mercury with 114 of sulphur, and digesting the product with a solution of potassic hydrate at 120° F. (48·9° C.) (red variety of HgS.)

[N.B.—On passing H_2S through a solution of a mercuric salt, a *white* precipitate is first formed. This results from a small quantity of the mercuric sulphide first produced forming a double salt with the mercuric salt in solution.]

Properties.—(a.) *Physical.* There are two varieties of this body, viz., black and red. The black is converted into the red variety without chemical change.

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The red salt, when heated, *air being excluded*, sublimes without fusing, the sublimate being black but becoming red on cooling; whilst, when heated *in the presence of air*, the sulphur burns off (as SO_2), and the metal is set free.

(*β.*) *Chemical.*—Mercurous sulphide is unaffected either by acids (except by nitro-hydrochloric acid), or by alkalies unless ignited in contact with them, when the mercury sublimes, and an alkaline sulphide and sulphate are formed—

$$4HgS + 8KHO = 4Hg + K_2SO_4 + 3K_2S + 4H_2O.$$

It forms compounds with metallic sulphides, and also with other mercuric salts. It is a very permanent body; hence its value as a paint.

Oxy-Salts.

(11.) Mercurous Sulphate (Hg_2SO_4) is a white, crystalline powder, formed on adding dilute sulphuric acid to mercurous nitrate, or by *gently heating* together mercury and sulphuric acid.

(12.) Mercuric Sulphate ($HgSO_4$) is a white powder, formed by heating together mercury and sulphuric acid *at high temperatures* ($Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O$).

Properties.—It is decomposed by pure water, the insoluble yellow basic salt, *trimercuric sulphate*, or *turpeth* (*turbith*) *mineral* being formed ($HgSO_4, 2HgO$), together with a soluble acid sulphate.

(14.) Mercurous Nitrate, or *Protonitrate of mercury;*

$$(Hg_2)''2NO_3, 2H_2O.$$

Preparation.—By digesting mercury in an excess of dilute nitric acid. If the mercury be in excess, a basic nitrate is formed, having the formula ($3(Hg_2)''2NO_3, Hg''_2O, H_2O$). This basic nitrate may be known from the neutral salt by its becoming black when triturated in a mortar with sodic chloride, calomel being formed, and mercurous oxide separated. Thus—

(*α.*) $(Hg_2)''2NO_3, 2H_2O + 2NaCl = Hg_2Cl_2 + 2NaNO_3 + 2H_2O.$

Normal mercurous nitrate + Sodic chloride = Calomel + Sodic nitrate + Water.

(*β.*) $3(Hg_2)''2NO_3, Hg''_2O, H_2O + 6NaCl = 3Hg_2Cl_2 + 6NaNO_3 + Hg_2O + H_2O.$

Basic mercurous nitrate + Sodic chloride = Calomel + Sodic nitrate + Mercurous oxide + Water.

(15.) Mercuric Nitrate ($2Hg''2NO_3, H_2O$).

Preparation.—By dissolving mercuric oxide (or metallic mercury) in an excess of nitric acid.

A yellow basic nitrate ($Hg2NO_3, 2'Hg'O, Hg''O$) is precipitated by the action of water upon mercuric nitrate, from which salt, by the continuous action of hot water, all the nitric acid may be removed, mercuric oxide only remaining.

Reactions of Mercury compounds.—(*See* Analytical Tables.)

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THALLIUM (Tl=204).

Atomic weight, 204. *Molecular weight (probable)*, 408. *Specific gravity*, 11·8 *to* 11·91. *Fusing point*, 561° F. (294° C.). *Atomicity, monad as in thallous compounds* (′) ($TlCl$; OTl_2), *and triad as in thallic compounds* (‴) ($Tl'''Cl_3$).

History.—Discovered by Crookes (1861), by means of its peculiar spectrum. This spectrum was first noticed in a deposit taken from a flue at a sulphuric acid manufactory, where thalliferous pyrites had been used in the manufacture of the acid. (Thallium is derived from θαλλός, "green," so named from its pecular spectrum.)

Natural History.—It occurs sparingly, but widely in some specimens of Spanish and Belgian pyrites, also in certain mineral waters, and in some specimens of mica and lepidolite.

Extraction.—By treating the deposit contained in the flues of sulphuric acid chambers with water, and precipitating the thallous chloride from the clear solution with hydrochloric acid. By the action of sulphuric acid, the thallous chloride may be converted into thallous sulphate, from which solution the metal may be precipitated by the action of metallic zinc or of the galvanic battery.

Properties.—(α.) *Physical.* A heavy crystalline body, exhibiting, when freshly cut, a brilliantly metallic surface. It is softer than lead, leaving a bluish line when rubbed on paper. This line may be known from a lead line, by its turning yellow (oxidising) after a short time. The metal crackles like tin when bent. It is diamagnetic. Its specific gravity varies from 11·8 to 11·91. Its specific heat is 0·0325. It is volatile at a red heat, and boils below a white heat. Its spectrum consists of one intensely green line. The salts of thallium are active poisons.

(β.) *Chemical.* Thallium rapidly tarnishes in air at common temperatures. When melted it rapidly oxidises, but it may be distilled in a current of hydrogen. It burns in oxygen, emitting a green light, and producing thallic oxide (Tl_2O_3). It combines energetically with the haloids, and also with sulphur and phosphorus. The action of both nitric and sulphuric acids upon it is energetic, whilst that of hydrochloric acid is very slight.

In chemical position, thallium is more closely allied to the monatomic metal silver, than to the alkaline metals. With the alkali metals it *agrees* in its atomicity, as well as in the solubility and alkaline reactions of its oxide (Tl_2O) and of its carbonate (Tl_2CO_3); but it *disagrees*, in that the metal may be preserved unaltered in water, and may be precipitated from its salts by zinc. With silver it agrees in the sparing solubility of its chloride, and in the insolubility of its sulphide, whilst it must also be remembered that silver oxide, like thallous

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oxide is slightly soluble in water, and that its solution is alkaline.

Compounds of Thallium.

SALTS.	Formula (General).	Formula (Constitutional).
1. Thallous oxide	Tl_2O	OTl_2
2. Thallic oxide	Tl_2O_3	$\begin{cases} TlO \\ O \\ TlO \end{cases}$
3. Thallous chloride	TlCl	TlCl
4. Thallic chloride	$TlCl_3$	$TlCl_3$
5. Sesquichloride of thallium	$Tl_4Cl_6 = TlCl_3,3TlCl$	
6. Dichloride of thallium	$Tl_2Cl_4 = TlCl_2,TlCl$	
7. Bromides analogous to chlorides		
8. Thallous iodide	TlI	
9. Thallic iodide	TlI_3	
10. Thallous sulphide	Tl_2S	
11. Thallic sulphide	Tl_2S_3	
12. Thallous carbonate	Tl_2CO_3	$COTlo_2$
13. Thallous nitrate	$TlNO_3$	NO_2Tlo
14. Thallous sulphate	Tl_2SO_4	SO_2Tlo_2
15. Thallic sulphate	$Tl'''_2(SO_4)_3 7H_2O$	
16. Thallous phosphates — Orthophosphates	H_2TlPO_4	
	HTl_2PO_4	
	Tl_3PO_4	
Pyrophosphates	$H_2Tl_2P_2O_7$	
	$Tl_4P_2O_7$	
Metaphosphate	$TlPO_3$	

(1, 2.)—The Oxides of Thallium.—Both *Thallous Oxide* (Tl_2O) and *Thallic Oxide* (Tl_2O_3), are basic oxides, and form soluble crystalline salts. The thallous oxide is formed whenever a freely-cut surface of the metal is exposed to the air, but on placing the tarnished metal in water the oxide layer is instantly removed. The solution is alkaline, and rapidly absorbs carbonic acid from the air. When electrolysed, it yields metallic thallium.

Thallic oxide (Tl_2O_3) is a dark red powder, and is formed when thallium is burnt in oxygen. It may be prepared as a hydrate ($Tl'''HO_2$ or Tl_2O_3,H_2O), by adding potassic hydrate to a solution of a thallic salt.

A *suboxide of thallium* is supposed to exist.

(3-6.) The Chlorides of Thallium.—There are four thallium chlorides. *Thallous chloride* (TlCl) is formed either by burning the metal in chlorine, or as a white curdy precipitate on adding a soluble chloride to a solution of a thallous salt. It dissolves (like $PbCl_2$) in boiling water. With platinic chloride it forms the double salt $2TlCl,PtCl_4$, and with ferric chloride, the compound $6TlCl,Fe_2Cl_6$.

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(10.) Sulphide of Thallium (Tl_2S) is formed either by adding hydric ammonic sulphide to a solution of a thallous salt, or by the action of sulphuretted hydrogen on a solution of the oxalate, acetate, carbonate, nitrate or sulphate of thallium.

(14.) Thallous Sulphate combines with aluminic sulphate to form an octahedral alum ($Al_2'''Tl_2(SO_4)_4,24H_2O$).

Reactions of the Thallium Compounds.

1. They all impart a green color to flame, and produce the spectrum peculiar to the metal (*vide supra*).

2. The metal is reduced whenever a thallous salt is ignited with a mixture of charcoal and sodic carbonate.

3. The metal is precipitated when a piece of zinc is placed in a solution of a thallous salt.

(A.) THALLOUS SALTS.—1. *Soluble chlorides* or *bromides;* a white ppt. of thallous chloride (TlCl), or of thallous bromide (TlBr).

2. *Soluble iodides;* a yellow ppt. of thallous iodide (TlI).

3. *Potassic chromate;* a yellow ppt. of thallous chromate.

4. *Platinic chloride;* a yellow ppt. of $2TlCl,PtCl_4$.

5. *Alkaline hydrates* and *carbonates;* no ppt. (*see* Reaction with thallic salts).

6. *Ammonic sulphide;* a brownish-black ppt. (Tl_2S), insoluble in excess.

(B.) THALLIC SALTS.—1. *Soluble chlorides* or *bromides;* no ppt.

2. *Alkaline hydrates and carbonates;* a brown gelatinous ppt. ($TlHO_2$).

3. *Oxalic acid;* a white ppt.

TUNGSTEN (W (Wolfranium)=184).

Atomic weight, 184. *Specific gravity*, 17·4. *Atomicity tetrad* (^{iv}), *as in Tungstous compounds* (WO_2), *and hexad* (^{iv}), *as in Tungstic compounds* (WO_3).

Natural History.—It occurs as Scheelite ($CaWO_4$) as Wolfram ($MnWO_4,3FeWO_4$), and as a tungstate of lead and of copper.

Preparation.—By reducing tungstic anhydride (WO_3) with charcoal at a white heat.

Properties.—A white, hard, brittle, infusible metal. Its alloy with steel is intensely hard, and permanently magnetic in a high degree. When finely powdered it burns in air. Tungstic acid is formed by the action upon the metal either of nitric acid or of aqua regia, or else by heating it with nitre, or by boiling it in an alkaline solution. It combines with chlorine when heated with it.

Oxides of Tungsten.—Tungsten forms three oxides, WO_2, (which does not form salts with acids), WO_3, and W_2O_5 (or WO_2,WO_3).

Tungstous Oxide (WO_2).—This is prepared by heating WO_3 in

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a stream of hydrogen. It is a brown powder, and burns in air, forming WO_3. It is an indifferent oxide.

Tungstic Oxide.—*Tungstic anhydride* (WO_3). (Called tungstic acid).

Preparation.—By igniting the residue left after treating calcic tungstate (Scheelite) with hydrochloric acid.

Properties.—A yellow powder, insoluble in water and in most acids, but soluble in alkalies. When a *hot* alkaline solution is neutralized with an acid, a *yellow* precipitate of tungstic acid (H_2WO_4) occurs, but when a *cold dilute* solution is similarly treated, a *white* precipitate of hydrated tungstic acid (H_2WO_4,H_2O) is formed. Tungstic acid reddens litmus, and is soluble in alkalies.

The Tungstates.—Tungstic acid, it will be seen, exists in two modifications:—

(α.) *Common tungstic acid* is of a yellow color, and insoluble in water. This variety forms both *normal* salts (M_2WO_4) and *acid* salts ($3M_2O,7WO_3$). Tungstate of soda (Na_2WO_4) is employed as a mordant in dyeing, and is also used for the purpose of rendering muslin uninflammable.

(β.) *Metatungstic acid* is a white body, soluble in water. The metatungstates are formed by the action of hydrated tungstic acid on the tungstates.

The oxide W_2O_5 is of a blue color, and is formed whenever an acid solution of tungstic acid is brought into contact with a bar of tin or zinc.

Several chlorides are known, viz., WCl_2, WCl_4, WCl_5, WCl_6.

Reactions of the Tungstates.

1. *Sulphuretted hydrogen* and *ammonic sulphide;* no ppt.
2. A *borax bead* in the reducing flame with compounds of tungsten becomes yellow, changing to red as it cools.
3. If to acidulated solutions a piece of zinc be added, the blue W_2O_5 is formed.

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SUPPLEMENT TO THE METALS.

GALLIUM (Ga).

[*Omitted from page* 347.]

Atomic weight, ? *Fuses at* 86·27° F. (30·15° C.). *Specific gravity* 5·935.

History.—Discovered by M. Lecoq de Boisbaudran (1875). Termed gallium from Gallia (France).

Occurrence.—It occurs associated with zinc in the zinc blende of Bensberg; also in the yellow transparent blende of Asturias, and in the brown blende of Pierrefitte. In smaller quantities it is found in cadmies from Corphalie. Zinc dross, and the Swedish brown blende, contain sensible traces of gallium.

Preparation.—By the electrolysis of a solution of the oxide in potassic hydrate.

Properties.—By the above process gallium may be obtained in a fused state. It has a silvery-white color. It continues in this superfused state for several days when allowed to remain at rest and carefully protected; but if any part of its surface comes into contact with a trace of solid gallium, a spot is seen to form, which rapidly spreads. On crystallising it assumes a bluish tint, and its lustre diminishes. Gallium may be liquefied by the heat of the hand. The solid metal may be cut with a knife, and is both flexible and malleable. Heated to bright redness in the presence of air, gallium does not volatilise, and merely oxidises superficially. When cold, the metal has only to be rubbed with a rod to restore it to its original brightness.

Gallium Chloride (Ga_2Cl_6) is a deliquescent substance, very soluble in water.

Gallium Sulphate is a non-deliquescent substance, and also very soluble in water.

Gallium Alum is colorless and limpid.

[*Vide* "Chemical News," April 20, 1877, *et seq.*]

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IRIDIUM (Ir.)

[*Omitted from page* 409.]

Atomic weight, 198. *Specific gravity*, 21·15. *Atomicity*, *dyad* (IrO); *tetrad* ($IrCl_4$), *and hexad; also a pseudo-triad.*

History.—Discovered by Smithson Tennant.

Derivation.—*Iris* the rainbow, from the varied tints of its compounds.

Natural History.—Found native in platinum ores. It also occurs as an alloy with osmium.

Preparation.—(1.) (*α.*) Chlorine is first passed over a heated mixture of the iridium alloy and sodic chloride, double chlorides of iridium and sodium ($2NaCl,IrCl_4$), and of osmium and sodium being formed.

(*β.*) The mass is now treated with boiling water, whereby these double chlorides are dissolved away from the insoluble portion.

(*γ.*) The concentrated solution is then distilled with nitric acid, which decomposes the double osmium salt, liberating the volatile osmic anhydride (OsO_4).

(*δ.*) The residual solution in the retort (which contains the iridium) is then treated with ammonic chloride, and the resulting dark red-brown precipitate of ammonic iridic chloride ($2NH_4Cl,IrCl_4$) ignited. In this way iridium is obtained in a spongy form. (Wöhler.)

(2.) Frémy prepares the metal from the potassic iridic chloride ($2KCl,IrCl_4$), formed by the action of potassic chloride on a solution of the metal in aqua regia ($IrCl_4$), by igniting it in a current of hydrogen.

Properties.—(*α.*) *Physical.* A hard, white and brittle metal. It crystallizes in cubes and also in six-sided prisms (*dimorphous*). The metal may be obtained in a finely divided state as a black powder, having properties similar to platinum black, by precipitating it with alcohol from a solution of the sulphate. It fuses when heated in the voltaic arc or in the oxyhydrogen jet.

The fused metal has a specific gravity of 21·15.

Its alloy with osmium has a specific gravity of 22·6.

(*β.*) *Chemical.*—The pure metal when in mass is unacted upon either by air, by heat, or by any acid. On the contrary, its alloy with platinum is soluble in aqua regia, whilst the finely divided metal when heated in air absorbs oxygen, forming Ir_2O_3, a black powder used for imparting an intense black to porcelain. The finely powdered metal is oxidized (but not dissolved as in the case of rhodium) by fusion with hydric potassic sulphate. It is also oxidised by fusion with sodic nitrate and sodic hydrate, the compound resulting being soluble in aqua regia, forming a deep black liquid

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containing the double sodic iridic chloride ($2NaCl,IrCl_4$). Iridium, like palladium, combines with carbon when heated in the flame of a spirit lamp.

Compounds of Iridium.

	Compounds.	Formula.	Molecular Weight.
Oxides.	Iridious oxide	$Ir''O$	214
	Iridic oxide	$'Ir'''_2O_3$	444
	Iridic dioxide	$Ir^{iv}O_2$	230
	Iridic hydrate	$Ir^{iv}Ho_4$	266
	Iridic anhydride	$Ir^{vi}O_3$	246
Chlorides.	Iridious chloride	$Ir''Cl_2$	269
	Iridic chloride	$'Ir'''_2Cl_6$	609
	Iridic tetrachloride	$Ir^{iv}Cl_4$	340
	(The iodides similar to the chlorides).		
Sulphides.	Iridious sulphide	$Ir''S$	230
	Iridic sulphide	$'Ir'''_2S_3$	492

Reactions.

(1.) *Sulphuretted hydrogen* first decolorizes a solution of $2NaCl,IrCl_4$, precipitating sulphur, and afterwards precipitates the brown Ir_2S_3.

(2.) *Ammonic sulphide*, reaction as above, the precipitated Ir_2S_3 being soluble in excess.

(3.) *Sodic or potassic hydrate*, a brownish black precipitate, the solution turning green, and when heated blue.

(4.) *Potassic chloride*, a dark brown precipitate ($2KCl,IrCl_4$).

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CHAPTER XVIII.

NOTES FOR PRACTICAL ANALYSIS.

I.—Introductory.

(1). The solution being a liquid, note its reaction to test paper.

An acid reaction indicates,	*An alkaline reaction indicates,*	*A neutral reaction indicates,*
A free acid.	A free alkali or alkaline earth	Water.
An acid salt.	A salt with an alkaline reaction.	A normal (neutral) salt.
A normal salt having an acid reaction.	An alkaline sulphide or cyanide.	

(2.) Evaporate a portion of the solution to dryness :—

(α.) If it leaves no residue, it may be simply water.

(β.) If it leaves a residue, proceed to examine the solid constituents as follows :—

EXAMINATION OF SUBSTANCES BY DRY METHODS.

A.—Heat the Dry Solid in a Glass Tube.

Results.	Indications.
1. No action	Absence of organic matter, of fusible and volatile substances, of hydrates, and of salts containing water of crystallisation.
2. Change of color ..	Charring indicates organic matter. If acetates be present, acetone is evolved, and a carbonate remains which may be known by its effervescing on the addition of HCl. If the body be yellow when hot, and white when cold=ZnO. If it be brown when hot, and yellow when cold=SnO_2. If it be reddish brown when hot, and yellow when cold=PbO. If it be orange red when hot, and yellow when cold=Bi_2O_3.
3. Substance sublimes	Yellow drops (sulphur, sulphides or hyposulphites). Yellow crystals (HgI_2 ; As_2S_3). White octahedral crystals (As_2O_3). White crystalline sublimate (oxalic acid). Black sublimate (HgS ; or, if with a violet vapor, iodine). White sublimate, yielding NH_3 when heated with potash ammonium salts). Melts, and yields a white crystalline sublimate ($HgCl_2$). Sublimes without melting (Hg_2Cl_2).
Sublimate treated with Na_2CO_3 and charcoal yields	(α.) Metallic globules, and a metallic mirror (mercury compounds). (β.) No globules, but a black shiny mirror (arsenicum compounds).

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Results.	Indications.
4. Gases are evolved having peculiar odor or other characteristics.	NH_3; (ammonium compounds). Frankincense odor (benzoic acid). Irritating fumes (succinic acid). White fumes and crystalline sublimate (oxalic acid). H_2S; (sulphides, sulphites, hyposulphites). [Tests.—(α.) Smell. (β.) Lead paper.] CS_2; (sulphocyanates). [Test.—Odor]. CN; (cyanogen compounds). [Test.—(α.) Odor. (β.) Burns with a red flame.] CO_2; (carbonates). [Test.—Whitens lime water]. CO; (oxalates and formates). [Test.—Burns with a blue flame]. N_2O_4; (nitrates of the heavy metals). [Tests.—Color; reddish brown]. SO_2; (sulphites and hyposulphites.) [Tests.—(α.) Odor. (β.) Acid reaction]. O; (peroxides; nitrates; chlorates). [Tests.—Supports combustion]. Cl; (chlorides of certain metals; chlorates; hypochlorites. [Tests.—(α.) Odor. (β.) Bleaches indigo. (γ.) KI and starch].

B.—Heat the Substance with the Blowpipe on a piece of Charcoal.

Result.	Indication of presence of
Decrepitates.	Numerous salts, such as NaCl, etc.
Deflagrates.	Nitrates, chlorates.
Fuses and is then absorbed by the charcoal.	Alkaline salts.

(α.) If a WHITE RESIDUE remains after heating with the blowpipe, moisten it with a drop of cobaltous nitrate and again heat.

Result.	Indication of presence of
Blue	Al_2O_3.
Pink	MgO.
Green	ZnO.

(β.) If a COLORED RESIDUE remains, heat a small portion in a clear borax bead.

In inner (reducing) flame.	In outer (oxidizing) flame.	Indication of presence of.
Blue	Blue.	CoO.
Red	Blue.	CuO.
Sherry red	..	NiO.
Colorless	Amethyst.	MnO.
Green	Reddish.	Fe_2O_3.
Green	Green.	Cr_2O_3.

(γ.) If a METALLIC RESIDUE remains when heated in the inner flame, note the characteristics of the bead as follows:—

[It may be necessary in this case, in order to effect perfect reduction, to heat the metal with KCy.]

(1.) A metallic non-volatile residue, without incrustation.

Characters of bead.	Indication of presence of.
Brilliant white; malleable	Ag.
Yellow	Au.
Red scales or globules	Cu.
Magnetic globules	Fe, Co, Ni.

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(2.) A metallic residue, with incrustation. (This incrustation is due to the volatility of the metal.)

Characters of bead.	Incrustation.	Indication of presence of
Malleable and marks paper ..	Reddish brown when hot, yellow when cold	Pb.
Bright; malleable	Yellow when hot; white when cold	Sn.
Brittle	Dark orange when hot; yellow when cold	Bi.
Brittle	White fumes and white incrustation (Sb_2O_3)..	Sb.
The metal reduced but instantly volatilized	White incrustation. Garlic odor	As.
Do. do. do.	Yellow when hot; white when cold	Zn.
Do. do. do.	Reddish brown	Cd.

C.—Heat a Portion of the Residue moistened with HCl on a Clean Platinum Wire in the Inner Blowpipe Flame.

Color of Flame.	Indication of presence of
Yellow	Na.
Violet	K.
Green	Ba.
Crimson	Sr or Li.
Red	Ca.
Bluish green..	Cu—B_2O_3.

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II.—Examination for Bases.

TABLE I.

Reactions of the Salts of the Alkaline Metals.

	Sodium* (Na=23).	Potassium (K=39·1).	Ammonium (NH_4) (?).	Lithium (Li=7).
(A.) Wet Reactions:—				
1. Sodic or potassic hydrate and heat	—	—	Alkaline vapors of NH_3. (*a.*) Ammonia smell. (*b.*) Turns turmeric paper brown, the color disappearing when the paper is warmed or left. (*c.*) White fumes with HCl of NH_4Cl.	—
2. Tartaric acid ($C_4H_6O_6$)	—	White crystalline ppt. ($KHC_4H_4O_6$) insol. in alcohol, sol. in hot water.	White ppt. ($NH_4HC_4H_4O_6$) in a concentrated solution of an ammonium salt on standing, sol. in excess of water and in ammonia.	—
3. Platinic chloride ($PtCl_4$) and HCl	—	Yellow crystalline ppt. ($2KCl,PtCl_4$) insol. in alcohol, slightly sol. in water. *On ignition*, Pt+KCl is left.	Yellow crystalline ppt. ($2NH_4Cl,PtCl_4$), insol. in alcohol. *On ignition*, Pt only is left, the NH_4Cl being volatile.	—
4. Carbazotic acid ($C_6H_3(NO_2)_3O$) ..	—	Yellow crystalline ppt.— ($C_6H_2K(NO_2)_3O$).	Yellow crystalline ppt.	—
5. Nessler's reagent; potassic solution of potassic mercuric iodide ($2KI,HgI_2$)	—	—	A brown precipitate, or coloration only if the quantity present be small (NHg_2I,H_2O).	—
6. Hydro-fluosilicic acid ($2HF,SiF_4$)	—	A white gelatinous ppt. ($2KF,SiF_4$).	—	—
7. Potassic metantimonate ($KSbO_3$).	White crystalline ppt. ($NaSbO_3$) in neutral or slightly alkaline solutions.	—	—	—
(B.) Dry Reactions:—				
1. Application of heat	Fixed.	Fixed.	Volatile.	—
2. Color imparted to flame	Yellow; Spectrum, yellow line at D.	Violet; Spectrum, one line in red and one in violet.	—	Brilliant crimson.

* All the sodium salts except the metantimonate are soluble in water.

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TABLE II.

A Solution may contain a Salt of Potassium, Sodium, Ammonium, and Lithium.

(A.) DETERMINE PRESENCE OF AMMONIUM.—Boil a small quantity of the solution with KHO or NaHO in a test-tube, and note (*a.*) the odor, (*β.*) the reaction on turmeric, and (*γ.*) the action with HCl of the fumes (NH_3) evolved.

(B.) If an ammonium compound be present, evaporate the solution to dryness and ignite, until ammoniacal fumes cease to be evolved. Allow the residue to cool; dissolve in water; filter if necessary.

[N.B.—The evaporation to dryness and ignition is not required in the absence of ammonium salts, but is rendered necessary if ammonium compounds be present, inasmuch as the ammonium reactions interfere with those of potassium.]

Test the solution on a *clean* platinum wire in the blow-pipe or Bunsen flame. A yellow color indicates **SODIUM.**	Add to the solution in a watch glass HCl and $PtCl_4$: Stir: a yellow precipitate indicates **POTASSIUM.**

(C.) For LITHIUM the ignited residue, previous to dissolving it in water, is to be digested in a mixture of ether and absolute alcohol. The flame produced when the filtrate is fired will be of a brilliant crimson color.

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TABLE III.

Reactions of the Salts of Barium, Strontium, Calcium, and Magnesium.

	Barium (Ba″=137).	Strontium (Sr″=87·5).	Calcium (Ca″=40).	Magnesium (Mg″=24).
(A.) WET REACTIONS:—				
1. Ammonia and ammonic carbonate. (NH_4Cl to be added to prevent the precipitation of Mg)	White ppt. ($BaCO_3$). Sol. in acids.	White ppt. ($SrCO_3$). Sol. in acids.	White ppt ($CaCO_3$). Sol. in acids; somewhat soluble in NH_4Cl when boiled.	No ppt. A soluble double chloride $2NH_4Cl, MgCl_2$ being formed.
2. Calcic sulphate	*Immediate* white ppt. ($BaSO_4$).	White ppt. ($SrSO_4$) *after standing.*	No ppt.	No ppt.
3. Dilute sulphuric acid..	*Immediate* white ppt. ($BaSO_4$) in strong and in dilute solutions, insoluble in HNO_3. (Precipitation interfered with by the presence of an alkaline citrate.)	White ppt. ($SrSO_4$). In very dilute solutions, ppt. not immediate. Insol. in alcohol or in a concentrated solution of $(NH_4)_2SO_4$, even when boiled.	White ppt ($CaSO_4$) in concentrated solutions. Soluble in a boiling solution of ammonic sulphate.	No ppt.
4. Ammonia and ammonic oxalate	White ppt. ($Ba''C_2O_4$) soluble in HCl and HNO_3.	White ppt ($Sr''C_2O_4$).	White ppt ($Ca''C_2O_4$) in very dilute solutions. Sol. in HCl and HNO_3; insol. in acetic and oxalic acids.	No ppt. in the presence of NH_4Cl.
5. Hydro-fluo-silicic acid	White crystalline ppt. (BaF_2, SiF_4). Insol. in alcohol.	No ppt.	No ppt.	No ppt.
6. Ammonia	No ppt.	—	—	White ppt. (MgH_2O_2). Soluble in NH_4Cl. (See above.)
7. Ammonia and hydric sodic phosphate (Na_2HPO_4)	A white ppt. ($BaHPO_4$). Sol. in acetic acid.	A white ppt. ($SrHPO_4$). Sol. in acetic acid.	A white ppt. ($Ca_3P_2O_8$). Sol. in acetic acid.	White crystalline ppt. ($Mg(NH_4)PO_4$). Insol. in ammonia, ammonic carbonate or chloride. Soluble in dilute acids.
8. Potassic chromate (K_2CrO_4)	Yellow ppt. ($Ba''CrO_4$) in dilute solutions. Soluble in HNO_3.	No ppt.	No ppt.	No ppt.
(B.) DRY REACTIONS:—				
1. In blow pipe flame, or in Bunsen burner, the flame is colored	Green.	Red.	Orange red.	No special color imparted to the flame. If the ignited residue be moistened with nitrate of cobalt and heated in the blow pipe flame, a pink-colored mass is obtained.

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TABLE IV.

A solution contains a salt of Barium, Strontium, Calcium, and Magnesium.

Add to the solution NH_4Cl (NOTE 1), NH_4HO and ammonic carbonate, until no further ppt. is formed; heat gently (NOTE 2); filter.

Precipitate=$BaCO_3$, $SrCO_3$, $CaCO_3$;—

Dissolve the ppt. in HCl, and evaporate to dryness;—

Dissolve a *small* portion of the residue in H_2O, and add to it a solution of $CaSO_4$.

PRECIPITATE IMMEDIATE	PRECIPITATE AFTER 10 MINUTES	NO PRECIPITATE
indicates the presence of *barium*, but strontium and calcium may also be present. We thus prove the presence of **BARIUM.**	indicates the *presence* of strontium, but calcium may also be present. The *absence* of barium is also indicated. We thus prove the absence of barium and the presence of **STRONTIUM.**	indicates the *absence* of barium and strontium, but calcium may be present. If no precipitate occurs with $CaSO_4$, dissolve the remainder of the residue in water, and add to the solution ammonia and ammonic oxalate. A white ppt. indicates **CALCIUM.**

If a ppt. occurs with $CaSO_4$, drench the remainder of the residue with methylated spirit; heat the mixture and filter.

INSOLUBLE =$BaCl_2$.	SOLUBLE PORTION *contains* $SrCl_2$ *and* $CaCl_2$.	
Test its power of imparting a green color to the Bunsen flame. This indicates **BARIUM.**	Add dilute H_2SO_4 until no further ppt. is formed; filter and wash; boil the ppt. with a concentrated solution of ammonic sulphate; filter and wash the residue;—	
	INSOLUBLE PORTION =$SrSO_4$.	SOLUBLE PORTION =$CaSO_4$.
	Heat the residue, moistened with HCl, on a platinum wire in the Bunsen flame, when a crimson color indicates the presence of **STRONTIUM.**	Add NH_4HO and ammonic oxalate. A white ppt. indicates **CALCIUM.**

Filtrate contains magnesium.

Prove the complete precipitation of Ca, Sr, and Ba, by adding a drop of a solution of ammonic carbonate.

Add NH_4Cl, ammonia, and sodic hydric phosphate.

A white crystalline ppt. indicates

MAGNESIUM.

NOTES. 1.—The ammonic chloride is added to prevent the precipitation of the magnesia by the ammonia which is subsequently added.
2.—The mixture is *not* to be boiled, otherwise the ammonic chloride will dissolve a part of the ppt., especially if it be $CaCO_3$.

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TABLE V.

A Solution contains a Salt of Potassium, Sodium, Lithium, and Magnesium.

Divide the solution into two parts, one part consisting of about two-thirds of the whole.

Smaller portion.	Larger portion.
Add NH_4Cl, NH_4HO and Na_2HPO_4. A white ppt. indicates **MAGNESIUM.**	Evaporate to dryness and ignite. 1. Test a portion of the residue in the flame. A yellow color indicates **SODIUM.** 2. Digest the residue with a mixture of absolute alcohol and ether, and filter. The filtrate, when fired, burning with a crimson flame indicates **LITHIUM.** 3. Dissolve the residue from (2) in water, and add HCl and platinic chloride. A yellow ppt. indicates **POTASSIUM.**

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TABLE VI.

A Solution may contain a Salt of Barium, Strontium, Calcium, and Magnesium,

AND

A Salt of Sodium, Potassium, and Ammonium.

(A.) Test for an ammonium salt by heating with KHO. *Note.*—(α) smell, (β) action on turmeric, (γ) action with HCl on glass rod.

(B.) Add NH_4Cl, ammonia and ammonic carbonate until no further ppt. is thrown down. Heat gently and filter.

<table>
<tr>
<td rowspan="2">Precipitate is either
$BaCO_3$—$SrCO_3$—$CaCO_3$.
Wash thoroughly and proceed as in Table IV.</td>
<td colspan="3">Filtrate contains a
Compound of magnesium, sodium, and potassium.
Divide into two parts (1 and 2.)</td>
</tr>
<tr>
<td>1.
Add ammonic chloride, ammonia and hydric sodic phosphate.
A white crystalline ppt. indicates
MAGNESIUM.</td>
<td colspan="2">2.
Evaporate to dryness and ignite, in order to get rid of all compounds of ammonium.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.
Test a small portion of the residue in a Bunsen flame or on a platinum wire.
A yellow color indicates
SODIUM.</td>
<td>2.
Test a solution of the remainder of the residue with HCl and $PtCl_4$
A yellow crystalline ppt. indicates
POTASSIUM.</td>
</tr>
</table>

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TABLE VII.

Reactions of the Salts of Aluminium, Chromium, and Iron (Ferrous and Ferric.)

	Aluminium (Al=27·5) Al″ and Aliv.	Chromium (Cr=52·5). Cr″, Criv and Crvi.	Iron (Fe=56) as Feiv (ferric salts).	Iron (Fe=56) as Fe″ (ferrous salts).
(A.) WET REACTIONS:				
1. Ammonia (with or without NH_4Cl)	White ppt. of aluminic hydrate ($Al_2H_6O_6$); slightly sol. in excess; insol. if much NH_4Cl be present.	Green ppt. of chromic hydrate ($Cr_2H_6O_6$); sol. in excess, solution becoming pink.	Red ppt. of ferric hydrate ($Fe_2H_6O_6$); insol. in excess.	White ppt. of ferrous hydrate (FeH_2O_2), changing to green and then to red ($Fe_2H_6O_6$).
2. Ammonic carbonate ..	White ppt. of a basic carbonate.	Green ppt. of a basic carbonate.	Red ppt. ($Fe_2H_6O_6$) with evolution of CO_2.	Whitish green ppt. ($FeCO_3$), becoming red by exposure to air, forming a basic carbonate.
3. Potassic or sodic hydrate	White ppt. ($Al_2H_6O_6$), soluble in excess, $Al_2H_6O_6$ being reprecipitated by NH_4Cl.	Green ppt. ($Cr_2H_6O_6$) soluble in excess, solution becoming green, reprecipitated on boiling, or on adding NH_4Cl.	Red ppt. ($Fe_2H_6O_6$); insoluble in excess.	Green ppt. becoming red on exposure to air; insoluble in excess.
4. Ammonic sulphide ..	White gelatinous ppt. ($Al_2H_6O_6$) (H_2S is evolved).	Bluish green ppt. ($Cr_2H_6O_6$) when added in excess and the mixture heated; insol. in excess.	Black ppt. (FeS); sol. in dil. HCl, H_2S being evolved and white S left. (Note 5.)	Black ppt. (FeS) soluble in HCl, H_2S being evolved.
5. Sodic hydric phosphate ..	A white ppt. ($Al_2P_2O_8$) insol. in NH_4Cl; sol. in KHO.	—	A yellowish white ppt. ($Fe_2P_2O_8$). Ammonic acetate renders precipitation complete.	—
6. Potassic ferrocyanide (K_4FeCy_6)	—	—	Blue ppt. ($3FeCy_2, 2Fe_2Cy_6$); sol. in oxalic acid; decomposed by KHO.	Light blue ppt. ($K_2Fe''FeCy_6$), becoming dark Prussian blue ($3FeCy_2, Fe_2Cy_6$), insoluble in acids; decomposed by alkalies.
7. Potassic ferricyanide (K_3FeCy_6)	—	—	No ppt., but solution turns reddish brown.	Blue ppt. ($Fe''_3Fe''_2Cy_{12}$) (Turnbull's blue) insol. in HCl.
8. Potassic sulphocyanate (KCNS)	—	—	Blood red color, $Fe(CNS)_3$; color destroyed by $HgCl_2$, tartaric acid, etc.	No action.
(B.) DRY REACTIONS:				
1. Heat on charcoal	Blue colored mass (*Cobaltous Aluminate*) when moistened with cobaltous nitrate.	—	Minute magnetic spiculæ; sol. in HCl; solution giving a blue ppt. with K_4FeCy_6.	—
2. Heat on platinum foil with KNO_3 and Na_2CO_3 ..	—	A yellow mass (K_2CrO_4) formed, sol. in water; solution precipitated as $PbCrO_4$ with lead acetate.	—	—
3. Borax bead	—	Yellow in the inner and emerald green in the outer flame.	Yellowish brown in the outer flame and bottle green in the inner flame.	Similar to ferric salts.

NOTES.—1. Ammonic carbonate precipitates this group as well as Ba, Sr, and Ca compounds.
2. Potassic ferrocyanide serves to distinguish the presence of iron as a proto or ferrous salt.
3. To convert a ferrous into a ferric salt, boil the solution of the ferrous salt with a little nitric acid, or with HCl and a few crystals of $KClO_3$.
4. Ammonia, in addition to the above, also precipitates the phosphates of iron, chromium and aluminium, and the phosphates of the alkaline earths.
5. Sulphuretted hydrogen produces with a ferric salt a ppt. of sulphur, the ferric being reduced to a ferrous salt ($Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S$).

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TABLE VIII.

A Solution contains a Salt of Aluminium, Chromium and Iron (Ferric and Ferrous Salts).

1. Determine the absence of phosphates by heating with ammonic molybdate. The absence of a ppt. indicates the absence of phosphoric acid.
2. Test for a *ferrous salt* with potassic ferrocyanide, and for a *ferric salt* with potassic sulphocyanide.
3. If a ferrous salt be present convert it into a ferric salt by adding a little HCl and a few crystals of $KClO_3$; heat gently until any chlorous odor ceases to be evolved.

Add ammonic chloride and ammonia: heat gently.

The precipitate may contain—

$Al_2H_6O_6$ (*white*)———$Cr_2H_6O_6$ (*green*)———$Fe_2H_6O_6$ (*red*).

Filter immediately and wash the precipitate thoroughly. Wash the precipitate into an evaporating dish, and add an excess of KHO; boil for some time; and filter.

Precipitate consists of $Fe_2H_6O_6$ (red), and $Cr_2H_6O_6$ (green.)		Filtrate contains $Al_2H_6O_6$.
Fuse one portion of the ppt. on platinum foil with potassic nitrate and sodic carbonate. Act on the fused mass with boiling water and test the *yellow* solution with plumbic acetate; a yellow ppt. ($PbCrO_4$) indicates **CHROMIUM.**	Dissolve in HCl and add potassic ferrocyanide; a blue ppt. (Prussian blue) indicates **IRON.**	Add HCl in slight excess and then NH_4HO in *slight* excess. A white gelatinous precipitate indicates **ALUMINIUM.** [*Confirmatory test.*—Heat on charcoal with cobaltous nitrate.]

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TABLE IX.

A Solution contains a Salt of Aluminium, Chromium and Iron (Ferric and Ferrous Salts), and also Phosphates of the Metals of the Alkaline Earths.

1. Determine the presence or not of ferrous salts. If present convert them into ferric salts, by boiling with hydrochloric acid and potassic chlorate.

2. Determine the presence of phosphates in a fresh portion with ammonic molybdate and heat. A yellow ppt. of ammonic phospho-molybdate indicates phosphoric acid.

Add ammonia and ammonic chloride; heat gently; filter and wash thoroughly.

The precipitate may contain—

$Al_2H_6O_6$ and $Al_2P_2O_8$; $Cr_2H_6O_6$; $Fe_2H_6O_6$ and $Fe_2P_2O_8$; and also phosphates of baryta, strontia, lime and magnesia.

Dissolve in a little HCl and add KHO in excess; filter.

<table>
<tr><td colspan="3">Precipitate consists of iron ($Fe_2H_6O_6$) and the phosphates of the alkaline earths.</td><td colspan="3">Filtrate contains $Al_2H_6O_6$ and $Al_2P_2O_8$; and $Cr_2H_6O_6$.</td></tr>
<tr><td colspan="3">Digest with acetic acid; boil, and filter whilst hot.</td><td colspan="3">Boil for some time and filter.</td></tr>
<tr><td rowspan="3">Residue = $Fe_2P_2O_8$ indicates
IRON
(as a phosphate).</td><td colspan="2">Filtrate contains $Fe_2H_6O_6$ (that is, iron other than as phosphate) and the phosphates of the alkaline earths.</td><td>Precipitate $Cr_2H_6O_6$ (green.)</td><td colspan="2">Filtrate contains $Al_2H_6O_6$ and $Al_2P_2O_8$.</td></tr>
<tr><td colspan="2">Add citric acid and excess of ammonia; filter.</td><td rowspan="2">Fuse with Na_2CO_3 and KNO_3 on platinum foil. A yellow soluble mass indicates
CHROMIUM.
[Confirmatory test.—Acetic acid and Lead acetate.]</td><td colspan="2">Add a slight excess of acetic acid; boil, and filter whilst hot.</td></tr>
<tr><td>Precipitate=phosphates of the alkaline earths.</td><td>Filtrate contains iron.</td><td>Precipitate $Al_2P_2O_8$.</td><td>Filtrate $Al_2H_2O_6$.</td></tr>
<tr><td>Dissolve in HCl; add potassic acetate and Fe_2Cl_6 until the liquid remains red. Boil for some time, filter and test the filtrate for the
ALKALINE EARTHS.
Table IV.</td><td>Test with HCl and potassic ferrocyanide. A blue ppt. indicates
IRON
(not as a phosphate).</td><td>Indicates the presence of
PHOSPHATE OF ALUMINA.</td><td>Neutralise with ammonia. A white ppt. indicates
ALUMINA.</td></tr>
</table>

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	Manganese (Mn=55). ″, iv and vi.	Zinc (Zn″=65).	Nickel (Ni=58·8). ″ and iv.	Cobalt (Co=58·8). ″ and iv.
(A.) Wet Reactions:—				
1. Ammonic sulphide ..	*Flesh colored* ppt. (MnS); soluble in acetic and other acids.	*White* ppt. (ZnS); insoluble in acetic acid or in KHO; soluble in mineral acids.	*Black* ppt. (NiS); insoluble in acetic acid; soluble in excess of yellow ammonic sulphide.	Black ppt. (CoS); insoluble in acetic acid & in dilute HCl; soluble in aqua regia.
2. Sulphuretted hydrogen	Precipitation imperfect.	Precipitates ZnS from a solution of an acetate, or of a zinc salt containing an alkaline acetate, even if free acetic acid be present, and also if the solution of the zinc salt be neutral.	Precipitates NiS from a solution of an acetate or of a nickelous salt mixed with an alkaline acetate. No precipitate occurs in an acid solution.	A black ppt. (CoS) as above.
3. Ammonia	White ppt., turning brown by exposure to air (MnH_2O_2). The brown ppt. is insoluble in NH_4Cl.	White ppt. (ZnH_2O_2); soluble in excess.	Light green ppt. (NiH_2O_2) soluble in excess (solution blue); reprecipitated by KHO.	Blue ppt. (basic salt); soluble in excess (solution reddish brown).
4. Ammonia and Ammonic chloride	No ppt. ($2NH_4Cl, MnCl_2$ formed which is soluble.)	No ppt.	No ppt.	No ppt.
5. Sodic or potassic hydrate	White ppt. (MnH_2O_2); insol. in excess. Darkens by exposure from absorbing O.	White ppt. (ZnH_2O_2); soluble in excess, and in $(NH_4)HO$ and NH_4Cl.	Light green ppt. (NiH_2O_2); insoluble in excess.	Blue ppt. (basic salt); insoluble in excess. On boiling becomes CoH_2O_2.
6. Ammonic carbonate ..	White ppt. ($MnCO_3$) becoming brown.	White ppt. soluble in excess.	Green ppt. soluble in excess, forming a greenish blue solution.	Rose-red ppt. of basic carbonate; soluble in excess, forming a red solution.
7. Potassic cyanide	White ppt. ($MnCy_2$); soluble in excess.	White ppt. ($ZnCy_2$); soluble in excess.	Yellowish green ppt. ($NiCy_2$); soluble in excess, forming a brownish yellow solution ($2KCy, NiCy_2$). The $NiCy_2$ may be reprecipitated by a dilute acid. The double salt is decomposed by NaClO, $Ni_2H_6O_6$ being precipitated.	Red brown ppt. of $CoCy_2$; soluble in excess forming $2KCy, CoCy_2$. This on boiling becomes $K_6Co_2Cy_{12}$, which is neither reprecipitated by HCl, nor decomposed by NaClO.
8. Potassic ferro-cyanide..	White ppt.	Yellowish white ppt.	Greenish white ppt.	Dark green ppt.
(B.) Dry Reactions:—				
1. Borax bead	Outer flame, amethyst; inner flame, colorless.	——	Outer flame, sherry red; inner flame, grey (from reduced Ni).	A blue glass either in the outer or inner flame.
2. Fused with sodic carbonate and potassic nitrate	Green sodic and potassic manganate.	——	——	——
3. Heated on charcoal with sodic carbonate in the inner blow-pipe flame	——	Becomes yellow when hot, white when cold. Turns green when moistened with cobaltous nitrate and heated.	A grey metallic powder, attracted by the magnet, producing a green solution when dissolved in HNO_3.	A grey or white metallic powder, attracted by the magnet; soluble in HNO_3 producing a reddish-colored solution.

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TABLE XI.

A Solution contains a Salt of Zinc, Manganese, Nickel, and Cobalt.

Add ammonic sulphide in excess. Filter rapidly (to prevent the oxidation of the sulphides) and wash the ppt. with water containing $(NH_4)_2S$. The ppt. may contain

ZnS (white)——MnS (flesh colored)——NiS (black)——CoS (black).

Boil the precipitate in acetic acid and filter.

<table>
<tr><td>Filtrate contains manganese acetate.</td><td colspan="3">Precipitate contains ZnS (white) and NiS and CoS (black).</td></tr>
<tr><td>Add NH_4Cl, ammonia and ammonic sulphide; a flesh colored ppt. indicates
MANGANESE.
Confirm the presence of manganese by fusion with potassic nitrate and sodic carbonate on platinum foil.</td><td colspan="3">Dissolve in the least possible quantity of nitric acid, and add NaHO in excess and filter.</td></tr>
<tr><td></td><td>Filtrate contains Zinc (ZnH_2O_2).</td><td colspan="2">Precipitate consists of NiH_2O_2 and CoH_2O_2.</td></tr>
<tr><td></td><td>Pass H_2S through the solution. A white ppt. (ZnS) indicates
ZINC.</td><td colspan="2">Dissolve in HCl and add a few crystals of $KClO_3$; heat until all chlorous odor disappears. Neutralise the solution with Na_2CO_3. Add KCy until the precipitate first formed is redissolved. Boil, and when cold add a strong solution of sodic hypochlorite. After standing for some time, filter.</td></tr>
<tr><td></td><td></td><td>A black ppt. ($Ni_2H_6O_6$) indicates
NICKEL.
(Confirm by bead expt).</td><td>Filtrate contains Cobalt, as $K_6Co_2Cy_{12}$.
Evaporate to dryness and test by borax bead; a blue color indicates
COBALT.</td></tr>
</table>

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TABLE XII.

Reactions of the Salts of Copper, Bismuth, and Cadmium.

	Copper (Cu=63·5). As cupric salts, Cu″.	Bismuth (Bi=208).	Cadmium (Cd=112).
(A.) WET REACTIONS:—			
1. Sulphuretted hydrogen (group reagent)	Brownish black ppt. (CuS); sol. with decomposition, in nitric acid and in potassic cyanide; insol. in ammonic sulphide.	Brownish black ppt. (Bi_2S_3); sol. in strong HNO_3; insol. in ammonic sulphide.	Yellow ppt. (CdS); sol. in hot dilute HNO_3, and in cold dilute H_2SO_4; insol. in ammonic sulphide and in potassic cyanide.
2. Ammonic sulphide	Brownish black ppt. (CuS).	Ditto.	Ditto.
3. Sodic and potassic hydrates	Light blue ppt. (CuH_2O_2); insol. in excess, turns black on boiling ($3CuO,H_2O$). In presence of grape sugar, etc., the ppt. dissolves, forming a blue solution, which on boiling precipitates cuprous oxide (Cu_2O).	White ppt. (BiH_3O_3); insol. in excess, becoming yellow on boiling (Bi_2O_3).	A white ppt. (CdH_2O_2); insol. in excess.
4. Ammonic hydrate .. .. .. or 5. Ammonic carbonate	Greenish blue ppt. (basic salt); soluble in excess to form a deep blue solution (cupr-ammonic hydrate).	White ppt. of BiH_3O_3 with NH_4HO, and of a basic carbonate with $(NH_4)_2CO_3$; insol. in excess.	White ppt. of CdH_2O_2 with NH_4HO, and of $CdCO_3$ with $(NH_4)_2CO_3$; insol. in excess.
6. Sodic carbonate	A greenish-blue ppt., becoming black ($3CuO,H_2O$) on boiling; soluble in ammonic hydrate.	White ppt., as with $(NH_4)_2CO_3$.	Same ppt. as with $(NH_4)_2CO_3$.
7. Potassic cyanide	Greenish-yellow ppt. ($CuCy_2$); sol. in excess. (No ppt. occurs when this solution is treated with H_2S).	White ppt.; insol. in excess.	White ppt. ($CdCy_2$); sol. in excess. (A ppt. occurs when this solution is treated with H_2S.)
8. Potassic ferrocyanide	Reddish-brown ppt. (Cu_2FeCy_6); insol. in dilute acids; decomposed by alkaline hydrates, $3CuO,H_2O$ being separated.	Light yellow ppt.	White ppt.
9. Potassic chromate ($K_2Cr_2O_7$)	Brick-red ppt.; sol. in NH_4HO, forming a green solution.	Yellow ppt. of basic chromate; sol. in dil. HNO_3; insol. in KHO. (Distinguish from lead.)	Slightly yellow ppt.; sol. in NH_4HO.
10. Sulphuric acid	No ppt.	No ppt. (Distinguish from lead.)	No ppt.
11. Potassic iodide	Grey ppt.	A brown ppt. (BiI_3).	A white ppt.
(B.) DRY REACTIONS:—			
1. Heated on charcoal with sodic carbonate	Red bead; sol. in HNO_3, giving a reddish-brown ppt. with K $FeCy_6$.	A brittle bead, with a dark orange incrustation when hot, becoming yellow when cold.	Forms a reddish-brown incrustation.
2. Borax bead	Blue glass. A trace of tin turns the bead a red color, owing to formation of Cu_2O.	Yellow when the bead is hot, and colorless when cold.	Yellow when the bead is hot, colorless when cold.

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TABLE XIII.

Reactions of the Salts of Tin (Sn'' & Sn^{iv}), *Antimony* (Sb''' & Sb^{v}), *and Arsenic* (As''' & As^{v}).

	Tin ($Sn''=118$). As stannous salts (1) (3).	Tin ($Sn^{iv}=118$). As stannic salts (2) (3).	Antimony ($Sb'''=122$). As antimonious salts (6).	Antimony ($Sb_{v}=122$). As antimonic salts (6).	Arsenic ($As'''=75$). As arsenious salts (8) (9).	Arsenic ($As^{v}=75$). As arsenic salts (8) (9) (10).
(A.) WET REACTIONS. 1. Sulphuretted hydrogen ..	A dark brown ppt. (SnS); *insol. in* NH_4HO; insol. in the normal, but sol. in the *yellow* ammonic sulphide, and repptd. as SnS_2 on adding HCl; sol. in KHO and NaHO.	A yellow ppt. (SnS_2); *sol. in* NH_4HO, in alkaline sulphides, in KHO, and in HCl.	Orange red ppt., Sb_2S_3; sol. in $(NH_4)_2S$, and in KHO; reppd. by HCl; very slightly sol. in NH_4HO, and insol. in ammonic carbonate; sol. in boiling HCl, forming $SbCl_3$ (5).	Orange ppt. (Sb_2S_5, mixed with S and Sb_2S_3); sol. in alkaline sulphides and hydrates; sol. in boiling HCl, with evolution of H_2S and precipitation of S.	A yellow ppt. (As_2S_3); sol. in alkaline hydrates, carbonates (=alkaline arsenite) and sulphides (=alkaline sulpharsenites) repptd. by HCl, or by HNO_3; nearly insol. in boiling HCl; sol. in boiling HNO_3.	A yellow ppt. (As_2S_3+S), sol. in $(NH_4)_2S$, NH_4HO and in ammonic carbonate.
2. Ammonic sulphide	A dark brown ppt. (SnS); sol. in excess.	Yellow ppt. (SnS_2); sol. in excess.	Orange red ppt. (Sb_2S_3); sol. in excess.	Orange ppt. (Sb_2S_5, S, and Sb_2S_3); sol. in excess.	Yellow ppt. (As_2S_3); sol. in excess.	Yellow ppt., soluble in excess.
3. Sodic and potassic hydrates..	White ppt. ($2SnO,H_2O$); sol. in excess (K_2SnO_2).	White ppt. (SnO_2,H_2O); sol. in excess and in HCl (4).	White ppt. (Sb_2O_3) (12); sol. in excess, potassic antimonite being formed.		No ppt.	No ppt.
4. Ammonic hydrate	White ppt ($2SnO,H_2O$); insol. in excess; sol. in KHO or NaHO.	White ppt. (SnO_2,H_2O); sparingly sol. in excess (precipitation prevented by tartaric acid); sol. in KHO.	White ppt. (Sb_2O_3) (12), insol. in excess; sol. in KHO.		No ppt.	No ppt.
5. Ammonic carbonate	White ppt. ($2SnO,H_2O$); insol. in excess; sol. in KHO.	White ppt (SnO_2,H_2O); sol. in KHO or NaHO.	White ppt. (Sb_2O_3).		No ppt.	No ppt.
6. Marsh's Test—By setting free hydrogen in the presence of the metal.	—	—	SbH_3 is evolved, when H is set free, by the action of Zn on H_2SO_4, but not by the action of Zn on KHO. *Tests for* SbH_3.—(α.) Passed through a solution of $AgNO_3$, precipitates a compound of Ag and Sb ($3AgNO_3+SbH_3=3HNO_3+Ag_3Sb$). (11). ($\beta$.) Flame bluish green. ($\gamma$.) Mirrors of metallic Sb are formed either on a cold piece of porcelain held in the SbH_3 flame, or in the glass tube through which the SbH_3 is passing, very near the spot at which the flame of a spirit lamp is applied. These deposits are insoluble in a solution of bleaching-powder, or of sodic hypochlorite.		AsH_3 is evolved when H is set free either by the action of Zn on H_2SO_4, or of Zn on KHO. *Tests for* AsH_3.—(α.) Passed through solution of $AgNO_3$, precipitates metallic silver, the solution containing As_2O_3 ($6AgNO_3+AsH_3+3H_2O=6HNO_3+3Ag_2+AsH_3O_3$). ($\beta$.) Flame bluish-white; white fumes being apparent above the flame of As_2O_3. (γ.) Mirrors of metallic As formed either when a cold piece of porcelain is held in the AsH_3 flame, or on the glass tube through which the AsH_3 is passing, at some distance from the point at which flame is applied These metallic mirrors are soluble in a solution of bleaching-powder or of sodic hypochlorite.
7. Reinsch's Test—By boiling a solution of the	—	—	Metal precipitated on the copper.		Grey film of As_2Cu_5 thrown down on the copper in dilute HCl solutions. Confirm presence of metal	Grey film thrown down on the copper in concentrated HCl solutions, but not in dilute HCl solutions.

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plate			—	No ppt.	A white crystalline ppt. of $MgNH_4AsO_4$, in the presence of NH_4HO and NH_4Cl.
9. Ammonio argentic nitrate	With an excess of $SnCl_2$, a black ppt. of metallic Hg.	—	—	A yellow ppt. (Ag_3AsO_3); sol. in NH_4HO, NH_4Cl and HNO_3.	A reddish-brown ppt. of triargentic arseniate (Ag_3AsO_4); sol. in NH_4HO and HNO_3.
10. Ammonio cupric sulphate	—	—	—	A yellowish green ppt. ($CuHAsO_3$), sol. in NH_4HO, NH_4Cl and HNO_3.	A greenish-blue ppt. of hydric cupric arsenate ($CuHAsO_4$) soluble in NH_4HO and HNO_3.
11. Auric chloride ($AuCl_3$) ..	With $SnCl_2$ a purple ppt. *(purple of Cassius).*	—	—	Ppt. of metallic gold from acid solutions.	
(B.) DRY REACTIONS.					
Fused on charcoal with sodic carbonate and potassic cyanide.	White malleable bead; sol. in HNO_3, the solution giving a white ppt. with $HgCl_2$. The bead has a yellow incrustation of SnO_2, which, when heated with cobaltous nitrate, becomes bluish green.		Brittle metallic bead; when heated in air gives off dense white fumes of Sb_2O_3, which incrust the globule. The bead is soluble in aqua regia ($=SbCl_5$); insol. in HCl, converted by HNO_3 into a mixture of Sb_2O_3 and Sb_2O_5, which is insol. in HNO_3, but sol. in a solution of tartaric acid.	[Heat the arsenical compound with C and Na_2CO_3 in a reduction tube.] A steel-grey mirror forms in the upper part of the tube, insoluble in HCl and oxidised by HNO_3. Heated in air forms As_2O_3. The metal is capable of complete volatilization (garlic odor).	

NOTES.—1. Stannous salts readily become stannic salts. Thus:—(α.) If $HgCl_2$ be mixed with $SnCl_2$, a white precipitate is first formed of Hg_2Cl_2, and when the mixture is heated, metallic mercury is precipitated, and $SnCl_4$ is formed.
(β.) $CuCl_2$ forms with $SnCl_2$, Cu_2Cl_2, and $SnCl_4$.
(γ.) Fe_2Cl_6 forms with $SnCl_2$, $FeCl_2$, and $SnCl_4$.
Stannous chloride, in a solution containing HCl, becomes, exposed to the air, stannic chloride and stannous oxychloride (Sn_2OCl_2).

2. Stannic is reduced to stannous chloride by the action of metallic tin or copper ($SnCl_4+Sn=2SnCl_2$).

3. A piece of zinc (but not Fe) precipitates metallic tin as a grey spongy mass upon the zinc from acid solutions of stannous and stannic salts.

4. Neutral salts (as Na_2SO_4) precipitate metastannic acid ($Sn_5O_{10},5H_2O$) from solutions of stannic salts when heated.

5. Water decomposes $SbCl_3$, a white insoluble antimonous oxychloride or powder of algaroth (SbOCl), soluble in tartaric acid being formed.
[NOTE.—The precipitate of BiOCl produced by the action of water on $BiCl_3$, is insoluble in tartaric acid.]

6. Antimony is precipitated from its solutions as a black powder by metallic zinc, iron, copper, lead, etc.

7. If an antimony solution be placed in a platinum dish, and a rod of zinc immersed in the solution, metallic antimony will be deposited on the platinum, at the spot where the zinc comes into contact with it. The metal is insoluble in cold HCl, but soluble in warm HNO_3.

8. Arsenious compounds act under certain circumstances as powerful reducing agents. Thus—
(α.) $2Cl_2+As_2O_3+5H_2O=As_2O_5,3H_2O+4HCl$.
(β.) $4AuCl_3+3As_2O_3+15H_2O=3(As_2O_5,3H_2O)+Au_4+12HCl$.
Also note that arsenious and arsenic compounds may act as oxidising agents, becoming themselves either reduced to a lower oxide, or to the metallic state.

9. For the distinctions between arsenious and arsenic compounds, see Reactions of Reinsch's Test, and magnesic sulphate.

10. Arsenic acid is reduced to arsenious acid by SO_2.

11. Filter the solution of the silver and proceed as follows with the precipitate and filtrate:—

Precipitate.
Wash with hot water, and boil in a strong solution of tartaric acid.
Filter; acidulate the filtrate with HCl, and pass H_2S through the solution.
An orange precipitate (Sb_2S_3) indicates antimony.

Filtrate.
Neutralize with NH_4HO.
(α.) If As be present, a yellow ppt. of arsenite of silver occurs (Ag_3AsO_3).
(β.) If Sb only be present, no ppt. is formed.

12. This precipitate does not occur with tartar emetic.

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TABLE XIV.

A Solution may contain a Salt of Lead, Mercury, Copper, Bismuth, and Cadmium; and also a Salt of Tin, Antimony and Arsenic.

Acidulate the solution with HCl and pass H_2S for some time through it. Heat gently.

The precipitate will consist of—

PbS, Black;	HgS, black;	CuS, black;	Bi_2S_3, black;	CdS, yellow;	and	SnS, brown;	SnS_2, yellow;	Sb_2S_3, orange red;	As_2S_3. yellow.

Wash the precipitate and boil with ammonic sulphide; filter.

Residue contains lead, mercury, copper, bismuth, and cadmium.

Dissolve in a little boiling nitric acid; dilute with water; add dilute H_2SO_4 until a ppt. ceases to be formed; when cold add to the solution an equal bulk of methylated alcohol; filter.

Residue contains lead and mercury.

Add tartaric acid and excess of ammonia. Boil; filter.

Residue HgS.	Filtrate contains $PbSO_4$.
Reduce with Na_2CO_3. A metallic mirror indicates **MERCURY** (as a mercuric salt)	Add potassic chromate. A yellow ppt. of plumbic chromate—($PbCrO_4$) indicates **LEAD.**

Filtrate contains bismuth, copper and cadmium.

Distil off the spirit from the solution; add excess of NH_4HO; boil and filter.

Precipitate BiH_3O_3 indicates **BISMUTH.** (Confirm by dissolving in a little HCl and adding a quantity of water to the dried residue.)	Filtrate contains Cu and Cd.

If copper be present the solution is blue. Add HCl in slight excess, and pass H_2S through the solution. Filter and wash the ppt. with H_2S water. Boil the ppt. with dilute H_2SO_4 and filter.

Black Residue CuS.	Filtrate Cd.
indicates **COPPER.**	Add NH_4HO and H_2S; a yellow ppt. of CdS indicates **CADMIUM.**

Filtrate contains tin, antimony and arsenic.

1. Add HCl, when the metals are reprecipitated as SnS_2, Sb_2S_3, and As_2S_3; filter and wash.
2. Digest the ppt. at a gentle heat with ammonic carbonate; filter.

Residue contains SnS_2 and Sb_2S_3

Dissolve in boiling HCl. Mix the acid solution with zinc in a Marsh's apparatus, in order to generate antimoniuretted hydrogen.

A metallic mirror formed when a cold piece of porcelain is held in the ignited gas indicates **ANTIMONY.**	If there is any metallic ppt. on the zinc, detach it, and dissolve it in HCl. Dilute with H_2O. Add $HgCl_2$; a grey ppt. of Hg or a white ppt. of Hg_2Cl_2 indicates **TIN.**

Solution contains arsenic.

Add HCl. A yellow ppt. of As_2S_3 indicates **ARSENIC.** (Reduce by heating in tube with charcoal and sodic carbonate.)

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TABLE XV.

Reactions of Salts of Lead, Silver and Mercury (as Mercurous and Mercuric Salts).

	Lead (Pb = 107). " and iv.	Silver (Ag = 108).	Mercury ('Hg' = 200). As Mercurous Salts. (NOTE 1.)	Mercury (Hg" = 200). As Mercuric Salts. (NOTE 1.)
(A.) WET REACTIONS:—				
1. HYDROCHLORIC ACID (group reagent)	White ppt. ($PbCl_2$); soluble in boiling water, or in an excess of cold water. The boiling solution deposits crystals on cooling; insoluble in ammonia.	White ppt. (AgCl); insol. in boiling water, sol. in ammonia, the AgCl being repptd. on adding an excess of HNO_3. Turns violet on exposure to light.	White ppt. (Hg'_2Cl_2 *calomel*); insol. in hot water; insol. in, but blackened by, ammonia (NH_2Hg_2Cl).	No ppt.
2. Sulphuretted hydrogen ..	Black ppt. (PbS) from acid solutions.	Black ppt. (Ag_2S) from acid solutions; sol. in dilute boiling HNO_3.	Black ppt. (Hg'_2S); insol. in dilute acids.	A white ppt. ($HgS,HgNO_3$), changing to yellow, then to brown (HgS and $HgCl_2$), becoming ultimately black (HgS); insol. in $(NH_4)_2S$, HCl, or HNO_3.
3. Sulphuric acid	White ppt. ($PbSO_4$); insol in water and in dilute acids, sol. in boiling HCl, in NaHO, and in an ammoniacal solution of tartaric acid.	No ppt.	No ppt., or a white ppt. if the mercury salt be in great excess.	No ppt.
4. Sodic or potassic hydrates ..	White ppt. (PbH_2O_2); sol. in excess, especially when heated.	Brown ppt. (Ag_2O). When heated, Ag_2O evolves O.	Black ppt. (Hg'_2O); insol. in excess.	Yellow ppt. (HgO); insoluble in excess.
5. Ammonia	White ppt. (basic salt); insol. in excess.	Brown ppt. (Ag_2O); sol. in excess.	Black ppt. of basic dimercurous ammonio nitrate; insol. in excess.	A white ppt. of a mercuric salt and mercuramide, called "white precipitate" ($NH_2Hg"Cl$).
6. Sodic or potassic carbonate ..	A white ppt. (basic carbonate); insol. in H_2O and KCy.	White ppt.; insol. in excess.	White ppt., becoming brown; insol. in excess.	Reddish-brown ppt.; insol. in excess.
7. Potassic iodide (KI)	Yellow ppt. (PbI_2); sol. in excess of KI, and in boiling H_2O; golden scales are pptd. as the water cools.	Yellow ppt. (AgI); insol. in dilute HNO_3, almost insol. in NH_4HO (AgCl is sol. in NH_4HO).	Green ppt.	Bright red ppt. (HgI_2); soluble in excess of KI or mercuric salt.
8. Potassic cyanide	A white ppt. ($PbCy_2$); insol. in excess, sol. in dilute HNO_3.	White ppt. (AgCy); sol. in excess and in NH_4HO, and in sodic hyposulphite; insol. in dilute HNO_3.	—	A white ppt. with mercuric nitrate (not with $HgCl_2$) of Hg_2y_2; sol. in excess.
9. Stannous chloride ($SnCl_2$) ..	—	—	A grey ppt. of metallic mercury.	White ppt. (Hg_2Cl_2) *calomel*; reduced to metallic state when boiled in excess of the reagent.
10. Potassic chromate (K_2CrO_4) .. and Potassic bichromate ($K_2Cr_2O_7$)	Yellow ppt. ($PbCrO_4$); sol. in KHO, insol. in acetic acid.	Dark red ppt. (Ag_2CrO_4).	Brick red ppt.	Reddish-yellow ppt. with K_2CrO_4, but no ppt. with $K_2Cr_2O_7$.
(B.) DRY REACTIONS:— Reduce on charcoal with Na_2CO_3	A malleable metallic bead with yellow incrustation of PbO when hot. The bead is sol. in HNO_3, the solution giving a white ppt. with H_2SO_4.	A bright malleable bead, without incrustation; sol. in NHO_3, the solution giving a white ppt. with HCl.	Instantly reduced and volatized. *Vide* NOTE 2.	Instantly reduced and volatized.

NOTES.—'. Mercurous and mercuric salts are oxidizing agents. When mercuric salts are employed for this purpose, mercurous salts are first formed, and finally the metal.

2. A slip of copper, placed in a solution of a salt of mercury, becomes rapidly coated with a grey stain of the metal. This stain becomes bright when rubbed, and may be volatilized by heat. Mercury salts, heated alone in a tube, either sublime *without decomposition* ($HgCl_2$; Hg_2Cl_2; HgS; HgI_2), or are decomposed. If the acid with which they are combined be a fixed acid (as CrO_3; P_2O_5, etc.), a fixed residue (as Cr_2O_3) remains.

Heat one part of a perfectly dry mercury salt with twelve parts of ignited sodic carbonate in a glass tube. The metal is reduced and sublimes. The sublimate appears like a grey coating, the particles combining, when slightly shaken, to form a globule. Dissolve this globule in nitric acid, and test the solution for mercury.

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TABLE XVI.

A Solution contains a Salt of Lead, Silver and Mercury (as a Mercurous Salt).

Add hydrochloric acid (in excess) and heat very gently. The precipitate contains

$PbCl_2$———$AgCl$———$'Hg'_2Cl_2$.

Filter: Boil the precipitate in a quantity of water, and filter whilst hot.

<table>
<tr><td colspan="2">The residue contains $AgCl$ and $'Hg'_2Cl_2$.</td><td>Filtrate contains $PbCl_2$.</td></tr>
<tr><td colspan="2">Add an excess of ammonia and filter.</td><td rowspan="2">A white ppt. ($PbSO_4$) with sulphuric acid indicates
LEAD.</td></tr>
<tr><td>Residue (black) contains mercury.</td><td>Filtrate contains $AgCl$.</td></tr>
<tr><td>A metallic mirror and globules are formed when the black residue ($NH_2'Hg_2'Cl$) is heated with sodic carbonate in a glass tube. This indicates the presence of
MERCURY
(as a mercurous salt).</td><td>Add nitric acid in excess; a white ppt. ($AgCl$) indicates
SILVER.</td><td></td></tr>
</table>

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Complete Examination for Bases.

(A.)—*The Substance being a Solid, and neither a Free Metal nor an Amalgam;*

1. Examine the body by the dry methods already described (page 437).
2. Dissolve it, or as much of it as will dissolve, in water. (Note the reaction of the solution to litmus).
3. Treat the insoluble residue first with dilute HCl and boil; and afterwards with conc. HCl and boil.

[The solutions 2 and 3 may be mixed and examined together.]

4. Treat the residue insoluble in HCl, with HNO_3, and boil.
5. Treat any residue insoluble in HNO_3 with aqua regia.
6. Any residue insoluble in water and in acids is to be dried, mixed with four times its weight of a mixture of equal parts of K_2CO_3 and Na_2CO_3, and the mixture fused in a crucible. The fused mass is then to be boiled in water, and filtered. Proceed as follows:—

Residue.	*Filtrate.*
Contains the bases as carbonates. Dissolve this in HCl and examine in the ordinary way.	Examine for acids.

Note.—The insoluble residue may consist of $BaSO_4$, $SrSO_4$, $CaSO_4$, and $PbSO_4$; also of AgCl and $PbCl_2$; also of ignited SiO_2, Al_2O_3, Cr_2O_3, Fe_2O_3, SnO_2, and Sb_2O_4.]

(B)—*The Substance being a Metal;*

I.—Dissolve in nitric acid diluted with water.
- (α.) Metals soluble with evolution of red fumes (Ag, Hg, Pb, Bi, Cu, Cd, As, Fe, Zn).
- (β.) Metals evolving red fumes but leaving a white insoluble residue (Sb, Sn).

II.—If the metal is insoluble in HNO_3, boil in HCl.

III.—Any residue insoluble in HCl, dissolve in aqua regia and test the solution for gold and platinum.

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TABLE XVII.

General Analysis.

1.—Test for ammonia in original material.
2.—The rare metals, as gold, platinum, etc., must be searched for separately.

No. 1. *Group reagent,* HYDROCHLORIC ACID. Add an excess of acid and filter. Notes 1, 2 and 4.	No. 2. *Group reagent,* SULPHURETTED HYDROGEN. Previous to passing the H_2S through the solution, dilute with water. Pass the H_2S through to saturation, and heat gently.	No. 3. *Group reagent,* AMMONIA. Evaporate filtrate from No. 2 to dryness after adding a little HNO_3. Dissolve the residue in HCl. Add a little water and filter off any undissolved SiO_2. Add ammonic chloride and then the ammonia. Notes 5 and 6.	No. 4. *Group reagent,* AMMONIC SULPHIDE. To filtrate add $(NH_4)_2S$ or pass H_2S through the filtrate containing ammonia from No. 3.	No. 5. *Group reagent,* AMMONIC CARBONATE. Add to the filtrate after boiling ammonic chloride and ammonic carbonate.	No. 6. *No Group reagent.*
Precipitate. AgCl white $PbCl_2$ white Hg_2Cl_2 white = Group 1. Examine by Table XVI.	*Precipitate.* PbS black HgS black CuS black Bi_2S_3 black CdS yellow } Insolulble in alkaline sulphides. SnS brown SnS_2 yellow Sb_2S_3 } orange Sb_2S_5 } As_2S_3 yellow } Soluble in alkaline sulphides. = Group 2. Examine by Table XIV.	*Precipitate.* $Al_2H_6O_6$ white $Fe_2H_6O_6$ red $Cr_2H_6O_6$ green $Al_2P_2O_8$ white Phosphates of alkaline earths } white = Group 3. Examine by Table IX. if phosphates be present, or by Table VIII. if no phosphates be present.	*Precipitate.* NiS black CoS black ZnS white MnS flesh colored = Group 4. Examine by Table XI.	*Precipitate.* $BaCO_3$ white $SrCO_3$ white $CaCO_3$ white = Group 5. Examine by Table IV.	Filtrate contains salts of $Mg''O$ Li_2O K_2O Na_2O = Group 6. Examine by Table V.

NOTES.—1. If the solution be a hydrochloric acid solution, pass on to No. 2.
2. Silicic, boric, benzoic and uric acids are also precipitated by HCl.
3. The presence of gold and platinum must be determined in the original solution.
4. Any precipitate occurring of oxychlorides may be disregarded, as these will be converted by H_2S into sulphides.
5. If organic matter is present, the residue must be ignited. Citric, tartaric, and other organic acids prevent the precipitation of the group.
6. The original solution should be tested for iron as a ferrous salt. If present, care must be taken that its conversion at this stage into a ferric salt is complete.

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III.—Examination for Acids.

1. *Test the substance as to its solubility in water.*

If the base be known, and the substance be found to be soluble, certain acids will be excluded, because the compounds are known to be insoluble. Thus, knowing baryta to be present, and finding the salt to be soluble, we know it cannot be sulphate of baryta, because that is insoluble. Or, conversely, knowing the base to be magnesia, and finding the salt to be insoluble, we know it cannot be a sulphate of magnesia, because that is soluble.

2. *Heat a portion of the finely-powdered substance in a test tube.*

Gas evolved.	Tests.	Source.
Oxygen.	Supports combustion.	Peroxides; nitrates; chlorates; etc.
SO_2	Odor. Blues starch and iodic acid.	Sulphites; hyposulphites.
N_2O_4	Reddish brown vapor.	Decomposition of the nitrates of the heavy metals.
CO_2	Renders lime-water turbid.	Carbonates.
CO	Blue flame.	Oxalates and formates.
CN	Odor. Burns with a rose flame.	Cyanogen compounds.
CS_2	Odor; gas combustible.	Sulphocyanates.
H_2S	Odor; blackens lead paper.	Sulphides; sulphites; hyposulphites.

3. *Heat a portion with two or three times its bulk of sulphuric acid.*

Acid.	Results.
Carbonic	Substance effervesces immediately; gas evolved whitens lime water.
Hydrochloric	Fumes irritating. The gas evolved turns white when ammonia is brought near it.
Acetic	Vinegar odor.
Sulphurous	Brimstone odor; blues starch and iodic acid.
Hyposulphurous (thio-sulphuric)	Brimstone odor, with the separation of sulphur.
Hydrosulphuric	Rotten egg odor; blackens lead paper.
Hydrofluoric	Irritating odor; corrodes glass.
Oxalic	Evolve CO, which burns with a lavender flame.
Cyanic	
Ferrocyanic	
Chromic	Evolves O; solution becomes brown.
Chloric	Evolves a greenish yellow explosive gas. [Further test—Precipitate any chloride present in a solution of the salt with $AgNO_3$; evaporate the clear filtrate to dryness; fuse the residue, whereby the chlorate is converted into chloride, and precipitate with argentic nitrate.]
Hypochlorous	Evolves the yellowish-green chlorine.
Hydriodic	Evolves violet vapors, which turn starch paper blue; solution turns dark colored.
Hydrobromic	Evolves reddish vapors, which turn starch paper yellow; solution turns red.
Nitrous .. .. .. [Also, under certain conditions, Nitric.]	Reddish-brown fumes. [Further test for nitrous acid—Mix a little of the solution with starch paste and KI; add to the solution a drop of H_2SO_4, when the blue iodide of starch is formed.]

[No action results with the following acids:—Sulphuric, phosphoric, silicic, boric, arsenic, iodic, and titanic.

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4. *Test for Nitric Acid.*

(α.) Dissolve a small portion of the substance in water, and add H_2SO_4 to set free the nitric acid. Float a solution of $FeSO_4$ on the surface of the mixture. A brown line at the junction of the liquids indicates nitric acid.

(β.) Add to the solution a little sulphindigotic acid to color it, and then H_2SO_4 and heat. If nitric acid be present, the indigo will be bleached. Chloric, bromic, iodic, and also nitrous, chlorous and hypochlorous acids, produce a similar reaction.

5. *Systematic Examination for Acids.*

Boil a considerable quantity of the substance with a slight excess of sodic carbonate. This removes all bases (other than the alkalies), as carbonates, basic carbonates, or oxides, the presence of which would interfere with many reactions (*e. g.*, $BaCl_2$ would precipitate Ag or Pb as well as H_2SO_4, etc.).

Filter off the precipitate, and boil the solution.

(A.) A preliminary examination of a small quantity, neutralized with nitric acid, and divided into two parts, is to be made as follows :—

<table>
<tr><th>A.—Add $BaCl_2$ or $Ba(NO_3)_2$.</th><th colspan="2">B.—Add $AgNO_3$.</th></tr>
<tr><td rowspan="2">Sulphuric ; white ppt., insol. in HNO_3.
Boric, Phosphoric, Silicic, Hydrofluoric, Sulphurous } White ppt. ; sol. in HNO_3.
Chromic ; yellow ppt., sol. in HNO_3.</td><td>Precipitates ; sol. in HNO_3.</td><td>Precipitates ; insol. in HNO_3.</td></tr>
<tr><td>Sulphurous, Boric, Silicic, Metaphosphoric } White ppts.
Phosphoric ; yellow ppt.
Chromic ; red ppt.</td><td>Hydrochloric ; white ppt. (sol. in ammonia).
Hydrobromic ; yellowish white pp. (slightly sol. in ammonia).
Hydriodic ; yellow ppt. (insol. in ammonia).
Hydrosulphuric ; black ppt.</td></tr>
<tr><td colspan="3">Boil the solution.
Sulphurous, Hyposulphurous (also Ferrous salts) } give black ppts. of reduced silver.</td></tr>
</table>

(B.) The remainder of the solution is to be divided into four parts, and treated as in the following table :—

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Part No. 1.

Portion acidulated with HCl.

[The acid is to be added until all CO_2 is evolved, and the solution after boiling remains very acid.]

Reagent.	Results.	Acid indicated.
$BaCl_2$	A white ppt.; insol. on boiling (1) (2)	H_2SO_4
Fe_2Cl_6	A deep blue ppt. (3)	H_4FeCy_6
,,	A brown color only (4)	$H_6Fe_2Cy_{12}$
,,	A blood red color (5)	CNHS

(1) A trace of Na_2SO_4 may have been present in the Na_2CO_3.
(2) $BaCl_2$ also gives a gelatinous ppt. with $2HF,SiF_4$. This ppt. is decomposed by strong acids, and when heated, SiF_4 is evolved.
(3) $FeSO_4$ gives a light blue ppt. with H_4FeCy_6.
(4) $FeSO_4$ gives a very dark blue ppt. with $H_6Fe_2Cy_{12}$.
(5) Color destroyed by $HgCl_2$, unaffected by HCl. [In this way the color may be known from that produced by the action of acetic acid on Fe_2Cl_6.]

Part No. 2.

Portion acidulated with HNO_3.

[Boil after the acid is added.]

Reagent.	Results.	Acid indicated.
$AgNO_3$(6)	A white ppt.; sol. in NH_4HO	HCl (1)
,,	A yellowish white ppt.; slightly sol. in NH_4HO	HBr (2) (3)
,,	A yellowish white ppt.; insol. in NH_4HO	HI (4)
,,	A white curdy ppt.; sol. in NH_4HO, and in alkaline cyanides.	HCy (5)

(1) If $HClO_3$ be present with HCl, ppt. the HCl with Ag_2SO_4; filter, add excess of Na_2CO_3, evaporate to dryness; ignite the residue; and add $AgNO_3$.
(2) Confirm the presence in the original solution by adding a little chlorine water and shaking up with ether.
(3) $AgBrO_3$ is sol. in water; AgBr is insol. On adding H_2SO_4 to a solution of $AgBrO_3$ a ppt. of AgBr is thrown down.
(4) $AgIO_3$ is sol. in ammonia, from which solution H_2SO_4 precipitates AgI. An iodate, unlike an iodide, is decomposed by acetic acid, setting free iodine.
(5) A cyanide (and that only) yields HCy with dilute H_2SO_4.
(6) H_4FeCy_6, $H_6Fe_2Cy_{12}$, and CNHS are also pptd. by $AgNO_3$, the ppts. being insol. in HNO_3. (These are detected in No. 1.)

For the separation of these acids *see* Table.

Note.—HF is not precipitated by $AgNO_3$.

Part No. 3.

Portion acidulated with acetic acid (1).

Reagent.	Results.	Acid indicated.
$CaCl_2$	A white gelatinous ppt. (2) (CaF_2)	HF
$CaSO_4$	A white ppt.	Oxalic (3)
$Pb(C_2H_4O_2)_2$	A yellow ppt.	Chromic
Fe_2Cl_6	A yellowish white ppt. (4)	Phosphoric

(1) Boiling with Na_2CO_3 only partially decomposes the phosphates of the alkaline earths. Hence examine the original solution for phosphoric acid with ammonic molybdate.
(2) A similar reaction occurs with sulphuric. The power therefore of the vapor given off when the ppt. is heated with hydric potassic sulphate to corrode glass must in all cases be tested.
(3) Calcic oxalate when ignited leaves $CaCO_3$, which dissolves with effervescence in acetic acid.
(4) This reaction is evidence only of the presence of a sol. phosphate, or of a phosphate decomposed by Na_2CO_3.

Part No. 4.

Portion rendered neutral.

[Add a slight excess of HNO_3; boil; and exactly neutralize with ammonia.]

Reagent.	Results.	Acid indicated.
$CaCl_2$	White ppt.; sol. in NH_4Cl & KHO (1)	Tartaric
,,	White ppt. after NH_4HO has been added and the solution boiled	Citric
Fe_2Cl_6	A pale yellow ppt.	Benzoic
,,	A reddish brown ppt.	Succinic

(1) This reaction is valueless in the presence of sulphuric, oxalic, hydrofluoric, phosphoric, arsenic, carbonic, boric, and sulphurous acids, all of which are precipitated by $CaCl_2$ in a neutral solution.

(*See* Organic Acids for special tests.)

For reactions of special acids free and in combination *see* Index.

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A Solution contains Hydrochloric, Hydrobromic, Hydriodic, and Hydrocyanic Acids.

A. To a portion (about one-third of the whole) add $AgNO_3$; collect and wash the ppt.
Boil with dilute HCl and place over the vessel on a glass plate;—*first* a drop of $AgNO_3$ solution, and *secondly* a drop of a solution of potassic hydrate.
(1.) The argentic solution becomes white (AgCy); sol. in ammonia.
(2.) The potassic hydrate solution is to be touched with a mixed solution of a ferric and ferrous salt, when a greenish blue ppt. is formed, which on the addition of HCl leaves Prussian blue.

These reactions indicate **HYDROCYANIC ACID.**

B. To the remainder of the solution, add a solution of $CuSO_4$ and H_2SO_3 (=Cu_2SO_4); a dirty white ppt. of Cu_2I_2 insoluble in water, but soluble in NH_4HO indicates **HYDRIODIC ACID.**

C. Add sufficient NaHO to precipitate the iron and copper compounds present; filter; evaporate the filtrate to dryness. Divide the residue into two parts 1 and 2.

Part 1.	Part 2.
Add $K_2Cr_2O_7$ and H_2SO_4. A brownish red gas is evolved (chlorochromic acid; CrO_2Cl_2) which condenses to a red liquid, decomposed by water into chromic acid (which gives a yellow precipitate with a lead salt) and hydrochloric acid. This indicates the presence of **HYDROCHLORIC ACID.**	Add a little chlorine water and shake up with ether. A red solution indicates **HYDROBROMIC ACID.**

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SECTION III.—Organic Chemistry.

CHAPTER XIX.

Organic Compounds and Organised Bodies — Definition of Organic Chemistry — Organic Analysis — Ultimate Analysis — Vapor Density — Method of determining Vapor Densities — Proximate Analysis.

Distinction between an Organic Compound and an Organised Body.

By *an organic compound*, such, *e.g.*, as sugar, urea, etc., we mean a body of definite chemical constitution, exhibiting frequently, if solid, a crystalline structure, and possessing, if liquid, a fixed boiling point. Many organic compounds have been formed artificially.

By *an organised body*, such, *e.g.*, as tissue, we imply a solid non-crystalline substance, of a fibrous or cellular nature (*i.e.*, non-crystalline), suffering decomposition when heated, so that it can neither be liquefied nor vaporised intact. No organised bodies have been formed artificially.

Definitions of Organic Chemistry.

(1.) Organic chemistry was originally defined as "*the chemistry of compounds produced under the influence of a vital force*," that is, of a force residing only in the bodies of *living* plants and animals. Those who held this doctrine of a vital force, divided organic bodies into two classes:—

(α.) *Direct organic bodies;* that is, bodies like sugar, starch, etc., actually formed in the living plant or animal; and

(β.) *Indirect organic bodies;* that is, bodies formed from direct organic bodies, by chemical or physical means. Thus oxalates and formates were regarded as belonging to organic chemistry, because the formates were prepared from the oxalates, and the oxalates from starch. Similarly, olefiant gas and alcohol were considered organic, because olefiant gas was produced from alcohol, and alcohol was formed from sugar. Starch and sugar being *direct* organic bodies, the products derived from them were regarded as *indirect* organic bodies.

Recent researches, however, have shown that some organic bodies may be prepared artificially; we mean by that, without the medium of any organic body. Thus *cyanogen* may be obtained from sodic cyanide (NaCN), a salt which may be prepared by passing nitrogen over a heated mixture of carbon and sodic carbonate. Alcohol (as

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Berthelot has shown) and urea, may also be built up artificially from their elements; and so with many other substances. Hence "the vital force" scarcely serves to mark the division between organic and inorganic chemistry.

2. Organic chemistry was defined by Laurent as "*the chemistry of carbon and its compounds.*" All organic substances contain carbon, combined sometimes with hydrogen only, as in benzene (C_6H_6), and sometimes with nitrogen only, as in cyanogen (CN). Sometimes the carbon is combined with hydrogen and oxygen, as in sugar, alcohol, etc., and not unfrequently with nitrogen in addition, as, for example, in the vegetable alkalies. Heating a substance in a test-tube, to see whether it chars, is our usual rough test for an organic body, and unless the body be volatile without decomposing, the result is accurate.

To accept this definition, however, in its integrity, would involve our placing carbonic oxide (CO) and carbonic anhydride (CO_2) amongst organic compounds. To meet this difficulty, Frankland defines an organic body as "a substance where one or more atoms of the carbon of a molecule are *directly* combined with carbon, nitrogen or hydrogen." Thus he excludes carbonic anhydride, as a body in which the carbon is combined directly only with oxygen (O=C=O). Cyanic acid is an organic compound, because the carbon is directly combined with nitrogen (N≡C—O—H). The objection to this hypothesis is that it takes for granted our power of examining the internal atomic and molecular structure of bodies, whereas at present such an insight is nothing more than mere speculation.

3. Organic chemistry was defined by Liebig as "*the chemistry of compound radicals.*" But compound radicals, as we have already seen, are not unknown in mineral chemistry. Silver nitrate $Ag(NO_3)$, which consists of silver and the compound radical (NO_3), bears a close resemblance to silver acetate Ag ($C_2H_3O_2$), consisting of silver and the compound radical ($C_2H_3O_2$). Both salts part with their compound radicals when a soluble chloride is presented to them, to form AgCl. Again succinic acid

$$\left.\begin{matrix} H_2 \\ C_4H_4O_2 \end{matrix}\right\} O_2 (= C_4H_6O_4)$$

bears a close resemblance to sulphuric acid

$$\left.\begin{matrix} H_2 \\ SO_2 \end{matrix}\right\} O_2 (= H_2SO_4)$$

each body containing a compound radical.

But although the existence of compound radicals can scarcely be regarded as peculiar to organic chemistry, nevertheless their presence is a very striking characteristic of it.

By a compound *organic* radical we mean "a group of atoms containing one or more atoms of carbon of which one or more bonds are unsatisfied." (Frankland.) As in inorganic chemistry we have elements of different atomicities, so in organic chemistry we have

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radicals of different atomicities. For example, we find *univalent radicals*, such as methyle (CH_3), forming methylic chloride $(CH_3)'Cl$; *divalent radicals*, as ethylene (C_2H_4), forming ethylic chloride $(C_2H_4)''Cl_2$; *trivalent radicals*, as glycerile (C_3H_5), the radical of glycerine ($C_3H_5(HO)_3$), etc. Basic radicals are sometimes found combined with chlorous radicals, the whole body being in such case made up of compound radicals; as *e.g.*, in methylic acetate $C_2H_3O(OCH_3)$.

No mono-, tri-, or quinqui-valent radical can exist as a separate group, any more than a monad (as hydrogen), a triad, or a pentad element (as nitrogen) can exist as a separate atom.

Having seen that it is impossible to draw any exact line dividing organic from inorganic chemistry, we may here note one or two special characteristics of organic bodies:—

1. The principal elements entering into the composition of organic bodies are few, *viz.*, carbon, hydrogen, nitrogen, and oxygen; at the same time nearly, if not every element, found in the mineral kingdom, is also to be found in the organs of the plants or of the animals that serve to elaborate these compounds.

2. Although *the elements* of which organic bodies are formed, are, as we have said, few, nevertheless the *number of atoms* constituting a molecule is frequently very large. No organic compound is known containing only two atoms in a molecule, and only one, *viz.*, hydrocyanic acid (HCN), containing three. In sugar 45 atoms, and in margarin 217 atoms, make up the molecule of these bodies respectively.

(3.) Organic bodies are remarkable for their complicated and elaborate constitution. This depends on two circumstances: — (α), the frequent occurrence of compound radicals in organic bodies; and (β), the chemical characteristics of the four elements of which organic compounds are chiefly composed.

Respecting this latter point, *viz.*, the chemical values of the four elements of which organic bodies are chiefly composed, it is to be noted that carbon is a *tetrad;* nitrogen, a *triad;* oxygen a *dyad*, and hydrogen, a *monad*.

The tetravalent atomicity of carbon is important. It is regarded as "*fully saturated*" when it is combined either with 4 monads (as in CH_4), or with the equivalent of 4 monads, such as 2 dyads (as in CO_2); or 1 triad and 1 monad (as in CNH), etc.) It is regarded as "*not saturated*" in compounds that contain less than 4 monads or their equivalent, such as CO. Under slight physical influences, however, such as light, the non-saturated compound CO will combine with Cl_2, forming *phosgene gas* ($COCl_2$), in which compound the carbon is fully saturated.

But a carbon atom will also combine with a carbon atom. (Duplication.) Two separate carbon atoms possess 8 unsatisfied bonds, (four to each); when combined, however (forming a dicarbon atom), they have only 6 unsatisfied bonds, because it will be seen that one

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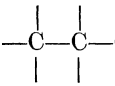
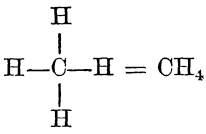
bond from one carbon atom combines with and satisfies one bond from the second carbon atom, thus satisfying 2 of the 8 bonds. Similarly, a combination of 3 carbon atoms (a tricarbon atom) has only 8 unsatisfied bonds instead of 12. Thus = a carbon atom; = a dicarbon atom;  = a tricarbon atom; Thus the addition of every carbon atom increases the non-saturated bonds of a compound, by 2. It will be seen, therefore, why we regard a series of bodies, that increase by an addition of CH_2, as an homologous series; as, for example, in the monatomic methyl series:

Methyl $(CH_3)'$	Methyl-hydride $(CH_3)H$	Methyl-chloride $(CH_3)Cl$	Methyl-alcohol $(CH_3)(HO$
Ethyl $(C_2H_5)'$	Ethyl-hydride $(C_2H_5)H$	Ethyl-chloride $(C_2H_5)Cl$	Ethyl-alcohol $(C_2H_5)(HO$
Propyl $(C_3H_7)'$	Propyl-hydride $(C_3H_7)H$	Propyl-chloride $(C_3H_7)Cl$	Propyl-alcohol $(C_2H_7)HO$
Etc.	Etc.	Etc.	Etc.

Types founded on carbon as the grouping agent in non-nitrogenized bodies, and on nitrogen in nitrogenized bodies. (Frankland.)

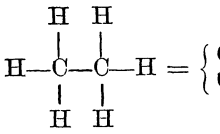
It may be conveniently noted here that Frankland regards these carbon groupings to which we have referred, as constituting a series of types of non-nitrogenous bodies, nitrogen forming a grouping element for nitrogenized bodies. Thus—

(1.) The *single carbon atom type* has been termed the *monadelphic* or *marsh gas type.*



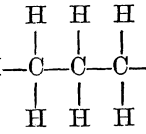
$H—C(H)(H)—H = CH_4$ Marsh gas.

(2.) The *dicarbon atom type* has been termed the *diadelphic* or *methyl type.*



$H—C(H)(H)—C(H)(H)—H = \begin{cases} CH_3 \\ CH_3 \end{cases}$ Methyl.

(3.) The *tricarbon atom type* has been termed the *triadelphic type.*



$H—C(H)(H)—C(H)(H)—C(H)(H)—H$ as for example $\begin{cases} CH_3 \\ CH_2{=}C_3H_8 \\ CH_3 \end{cases}$ Propyl-hydride,

and so on.

On the other hand nitrogenized bodies may be arranged under one of either of the following forms:—

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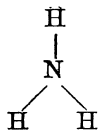
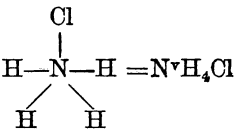
(4.) The *ammonia type*; represented thus—



$= N'''H_3$ Ammonia.

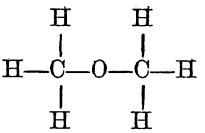
(5.) The *ammonic chloride type* represented thus—



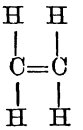
$=N^{v}H_4Cl$

Frankland also describes—

(6.) The *double monadelphic type.*



(7.) The *condensed diadelphic or olefine type.*



4. A great *variety of property* naturally occurs as the result of the complicated chemical constitution of organic bodies, some constituting our daily food, and others actively poisonous substances.

ORGANIC ANALYSIS.

The analysis of an organic body is of two kinds, viz., *proximate* and *ultimate.*

(1.) A *proximate analysis* of a body implies "the separation and estimation of its component or proximate principles"—

Thus: determining the presence and relative proportions of sugar, fat, casein, and salts in milk, constitutes "*a proximate analysis*" of milk.

(2.) An *ultimate analysis* of a body implies "the separation and the estimation of the constituent or ultimate elements"—

Thus: determining the presence and the relative proportions of carbon, hydrogen, nitrogen, and oxygen in the casein of the milk, constitutes "*an ultimate analysis*" of casein.

We commence our studies with the principles of, and the method of conducting, the ultimate analysis of organic bodies.

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ULTIMATE ANALYSIS OF ORGANIC BODIES.

The principle of an ultimate analysis of a body containing carbon, hydrogen, and oxygen, may be stated as follows, viz. :—To burn a known weight of the organic body in oxygen, and to collect and weigh the oxidised products. The *carbon* is determined as CO_2, the *hydrogen* as H_2O, and the *oxygen* by difference—that is, by subtracting the combined weight of the hydrogen and carbon from the total weight of the material operated upon.

The conditions necessary for the success of the experiment are as follows :—(1.) That the body operated upon should be *pure;* (2.) that it should be *dry;* (3.) that it should be perfectly burnt; and (4.) that the products should be accurately weighed.

The history of ultimate analysis.—The first attempts at organic analysis were simply destructive distillation, the *products* of such distillation being regarded by the older chemists as *the elements* of organic bodies. Thus grew the dictum "air, oil, water, and earth (caput mortuum) are the elements of organic bodies."

Hales and Priestly were the first who improved this process of destructive distillation by collecting the gaseous products evolved during the operation.

In 1810, Gay Lussac and Thénard suggested (in principle) the process of analysis which is now adopted, viz., burning the body in oxygen and collecting the products. Their process was as follows :—A glass tube, containing a weighed quantity of the organic body to be examined was placed in an upright position in a furnace. When the tube was sufficiently heated, oxygen was supplied to the organic matter by dropping potassic chlorate into the tube. The gases evolved were collected over mercury and *measured.*

The objections to this process were its practical difficulties, namely, (1.) the constant cracking of the tube, (2.) the frequent loss occasioned by the substance being blown out of the tube, (3.) the difficulty of ensuring the complete combustion of the organic matter owing to the immediate and rapid generation of oxygen from the potassic chlorate, and (4.) the inaccuracies resulting from measuring the products.

Berzelius suggested the following improvements in the process, viz. (1.) placing the tube in a *horizontal* position; and (2.) modifying the violent action of the potassic chlorate by mixing it with common salt. Further (3.), he *weighed* the products, using for this purpose a chloride of calcium tube to collect the water, and fragments of caustic potash contained in a large glass bulb to collect the carbonic anhydride.

Gay Lussac and Thénard, Berard, Berzelius, and, lastly, Thompson, suggested the use of cupric oxide, instead of potassic chlorate, for the supply of the oxygen. Its advantages were—(1.) the comparative ease with which it could be obtained pure and dry; and (2.), more

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particularly, that when heated alone it required a high temperature for its decomposition, but that, when heated with organic matter, it readily imparted its oxygen to it.

Lavoisier, Saussure and Prout suggested passing a stream of pure oxygen through the combustion tube instead of using cupric oxide.

Finally, Liebig improved the process in many of its details. He suggested the use of plumbic chromate as an oxidising agent, instead of cupric oxide, under the following circumstances—

(α.) *When the compound contains chlorine or bromine.* When cupric oxide is used, the volatile bodies $CuCl_2$ and $CuBr_2$ are formed, which, condensing in the calcic chloride tube, introduce a source of error. This is avoided by the use of plumbic chromate.

(β.) *When the compound contains sulphur.* The sulphur, when burnt with cupric oxide forms SO_2, which would be absorbed by the potassic hydrate solution, thus falsifying the results obtained by weighing the potash bulbs. With plumbic chromate, on the contrary, the sulphur does not form SO_2, but the non-volatile body plumbic sulphate.

(γ.) *When the compound contains alkaline salts.* The alkaline carbonates into which these alkaline salts are converted by heat, are not decomposed by contact with cupric oxide (thereby decreasing the quantity of free CO_2 formed), whilst they are decomposed by the action of plumbic chromate.

(δ.) When the compound is difficult of combustion.

(I.)—The Experimental Determination of the Carbon, Hydrogen, and Oxygen of an Organic Compound, not containing Nitrogen.

This is conducted as follows:—A tube of hard glass, eighteen inches long, and closed at one end, is filled for the first five inches with pure cupric oxide. An accurately-weighed quantity of the organic body to be examined, mixed with cupric oxide, is then introduced, the remainder of the tube being filled up with pure oxide. To this combustion tube is attached—

First, an accurately weighed tube, containing *calcic chloride*, for the purpose of absorbing the moisture, calcic chloride not absorbing carbonic anhydride; and

Secondly, an accurately weighed bulb-tube containing *a solution of potassic hydrate*, for the purpose of absorbing the carbonic anhydride formed during the experiment.

The front part of the combustion tube (that is, the part containing pure cupric oxide) is first heated to redness. This done, the heat is next applied to the mixture of the oxide and the organic matter, commencing at that part of the tube furthest from the absorption tubes. Thus the organic body is burnt by the oxygen of the cupric oxide. The hydrogen of the organic body, as water, will be absorbed by the

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calcic chloride, and the carbon as carbonic anhydride will be absorbed by the potash solution.

Finally, the sealed end of the combustion tube is broken off, and pure dry air or oxygen is drawn through the apparatus, so that any moisture or carbonic anhydride remaining in the tube unabsorbed may be displaced.

When the apparatus is cool, the tubes are again weighed. The increase in the weight of the chloride of calcium tube represents the water formed by the combustion of the hydrogen of the compound, and the increase in the weight of the bulbs containing the solution of potassic hydrate, represents the carbonic anhydride formed by the combustion of the carbon of the compound.

Determination of Oxygen.—The oxygen is calculated by difference; that is, having proved the body to contain only hydrogen, carbon, and oxygen, the combined weights of the hydrogen and the carbon are subtracted from the total weight.

Method of Calculating Results.

Say 10 grains of sugar is burnt :—

(α.) The calcic chloride tube after experiment weighed 205·78grs.
,, ,, before ,, ,, 200·00grs.

Therefore the product of the combustion of the hydrogen of 10 grains of sugar yields H_2O = 5·78grs.

It follows therefore—

H_2O : H_2 :: Wt. of H_2O in 10 grs. of sugar. : x = 0·643 grs. of hydrogen in 10 grs. of sugar.

18 : 2 :: 5·78 : x = 0·643 grs. of hydrogen in 10 grs. of sugar.

(β.) The potassic hydrate solution after expt. weighed 815·39grs
,, ,, ,, before ,, 800·00grs.

Therefore the product of the combustion of the carbon of 10 grains of sugar yields CO_2 = 15·39grs.

If follows therefore—

CO_2 : C :: Wt. of CO_2 in 10 grs. of sugar. : x = 4·198 grs. of carbon in 10 grs. of sugar.

44 : 12 :: 15·39 : x = 4·198 grs. of carbon in 10 grs. of sugar.

(γ.) 10 grs. — 4·854 grs. (0·643 grs. of H + 4·211 grs. of C) = 5·146 grs. of oxygen.

(δ.) Multiplying these quantities by 10, we find that there are in every 100 parts of sugar—

Carbon	41·98 parts.
Hydrogen	6·43 ,,
Oxygen	51·59 ,,

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Experimental errors.—Usually our estimation of the carbon in a body is 0·1 to 0·2 per cent. *too low*, the error arising from the incomplete combustion of the body, whilst our estimation of the hydrogen is 0·1 to 0·2 per cent. *too high*, arising from the impossibility of effecting the entire removal of moisture.

In the case of a liquid it is commonly placed in the combustion-tube in a glass bulb, the exact weight of the liquid introduced being previously determined; whilst in the case of a fat or wax, etc., a little glass boat is usually employed for the same purpose.

(II.)—Estimation of the Hydrogen and Carbon in a Body containing Nitrogen.

If the nitrogen be evolved as free nitrogen from the organic body, its presence would not signify, inasmuch as pure nitrogen would neither be absorbed by the calcic chloride, nor by the solution of caustic potash. But as a rule, during a combustion analysis, a small quantity of the nitrogen of nitrogenised bodies becomes oxidised to nitric oxide (N_2O_2), which, on coming into contact with the air in the potash-bulb apparatus, would be further oxidised to nitric peroxide (N_2O_4), and would then be absorbed by the solution of potassic hydrate, and so interfere with the estimation of the CO_2.

To remedy this it is usual to place some copper turnings in the front part of the combustion-tube, and to maintain the metal at a red heat during the whole experiment. The action of the copper is as follows:—The red-hot copper decomposes any oxide of nitrogen formed, itself absorbing the oxygen, and setting free pure nitrogen, which merely escapes into the air, unabsorbed either by the chloride of calcium or by the potassic hydrate.

(III.)—The Recognition and Estimation of the Nitrogen in an Organic Body.

The carbon and hydrogen of the substance having been first estimated by the process described above, the nitrogen is to be determined by a separate experiment.

(1.) The Recognition of Nitrogen in Organic Bodies.—The presence of nitrogen may be known,

(α.) By heating the substance with a small piece of potassium (or sodium), dissolving the residue in water, adding to the clear filtrate a few drops of a mixed solution of ferrous sulphate and ferric chloride and an excess of hydrochloric acid. A blue precipitate (Prussian blue) indicates the presence of nitrogen.

(β.) By the generation of ammonia when the organic body is heated with potassic hydrate.

(2.) Estimation of Nitrogen.—(α.) *By volume* (process of Dumas). This process is applicable to the analysis of all nitrogenised substances.

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The combustion-tube, sealed at one end, is prepared as follows: —The first five or six inches of the tube is filled with hydric sodic carbonate ($NaHCO_3$). The mixture of cupric oxide and the organic matter is next introduced, and afterwards some pure cupric oxide, the last two inches of the tube being filled up with copper turnings. A delivery-tube, the further end of which dips under mercury, is now fitted to the combustion tube. The apparatus having been proved to be air-tight, a portion of the hydric sodic carbonate is heated. The carbonic anhydride generated, sweeps the air out of the tubes. If this were not done the atmospheric nitrogen would vitiate the results. This done, a graduated tube filled two-thirds with mercury and one-third with a solution of potassic hydrate (the latter to absorb the CO_2 generated during the experiment), is inverted over the delivery-tube. The copper in the combustion-tube is now made red hot, so that it may effect the decomposition of any oxides of nitrogen formed during the process. The pure cupric oxide is next heated, and then the mixture of the cupric oxide with the organic matter. The H_2O formed is condensed, whilst the CO_2 is absorbed by the potassic hydrate solution, the nitrogen alone collecting in the receiver. The combustion being complete, the undecomposed carbonate is heated, the carbonic anhydride generated sweeping any residual nitrogen from the combustion and delivery-tubes into the graduated receiver.

The volume of nitrogen formed is then read off, and corrections having been made for moisture, for temperature, and for barometric pressure, its weight is estimated from the corrected volume.

A slight experimental error, not exceeding 0·3 to 0·5 per cent., arises from a trace of nitrogen remaining in the tubes, and also being retained within the pores of the copper.

(*β.*) (Process of Varrentrapp and Will.) We have noted that when nitrogenized organic matter is heated with sodic or potassic hydrates, the nitrogen is evolved as ammonia.* Advantage is taken of this reaction in estimating the nitrogen as follows:—

A known weight of the organic body is mixed with soda-lime. This is prepared by slaking lime (CaO) with a solution of sodic hydrate, and afterwards drying and igniting the product formed. The advantages of soda-lime over caustic soda are manifest. Caustic soda is very fusible, very deliquescent, very difficult to powder, and hence very difficult to mix with the organic body. Soda-lime, on the contrary, is infusible at a red heat, is not deliquescent, and, owing to the ease with which it can be reduced to a fine powder, admits of ready admixture with the organic body. The mixture of the organic matter with the soda-lime is now placed in a glass combustion tube, and heated.

* When a non-nitrogenized organic body is heated with potassic hydrate, the carbon of the organic matter burns at the expense of the oxygen of the water of the hydrate, the carbonic anhydride formed combining with the alkali, and the hydrogen escaping.

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The ammonia evolved is conveyed into a tube containing hydrochloric acid, and the quantity of ammonia collected estimated as ammonic platinic chloride ($(NH_4)_2PtCl_6$), which may be either collected and weighed on a balanced filter (100 grs. = 6·27 N), or else ignited in a crucible and the weight of the nitrogen estimated from the reduced platinum (100 grs. of Pt. = 14·18 N).

The ammonia may also be estimated by collecting it in a measured quantity of dilute sulphuric acid of known strength, the amount of acid unneutralized, being determined by titration (Peligot). This process of estimating the nitrogen as ammonia is not practicable, however, when the nitrogen is present as a nitro-compound, as, *e.g.*, in nitrobenzol, ethyl nitrate, etc., or in the case of certain alkaloids, etc.

(IV.)—The Estimation of the Sulphur, Phosphorus and Haloid Elements in an Organic Body.

(1.) Estimation of Sulphur.—This is effected by one or other of the following processes:—(α.) By igniting a known weight of the organic substance with a mixture of nitre and potassic hydrate. An alkaline sulphate is thus formed, the sulphur of which may be estimated by precipitating its solution with baric nitrate (100 grs. $BaSO_4$ =13·67 grs. of S.).

(β.) By interposing between the calcic chloride tube and the potash bulbs in the combustion apparatus, a tube containing lead oxide, the sulphurous acid formed combining with the lead oxide to form a sulphate of lead ($PbO_2+SO_2=PbSO_4$).

(The presence of sulphur vitiates the accuracy of the carbon determination, when cupric oxide is used as the oxidising agent. This does not occur when plumbic chromate is employed. *See page* 369).

(2.) Estimation of Phosphorus.—This may be effected in a similar manner to the process (α.) already described for the determination of sulphur. After precipitating the sulphuric acid as $BaSO_4$, the excess of barium is to be thrown down with dilute sulphuric acid. The phosphoric acid present, the form in which the phosphorus now exists, is then to be estimated by supersaturating the solution with ammonia and adding magnesic sulphate. The ammonic magnesic phosphate precipitated is then collected, ignited, and weighed as $Mg_2P_2O_7$ (100 grs.=27·92° P).

(3.) Estimation of Chlorine, Bromine, and Iodine.—This is effected by heating the organic body in a tube with quick-lime, whereby $CaCl_2$, or $CaBr_2$, or CaI_2, is formed. The product is then dissolved in dilute nitric acid, and the chlorine, bromine, or iodine precipitated with argentic nitrate.

(4.) Estimation of Chlorine, Bromine, Iodine, Sulphur, and Phosphorus in an Organic Body.—A mixture of three or four grains of the organic body with eighty grains of nitric acid (Sp. Gr.

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1·5), and a few crystals of argentic nitrate, contained in a sealed tube, is to be heated for three or four hours in an oil bath. When the tube is cold its contents are to be washed into a beaker. The insoluble AgCl, or AgBr, or AgI, which will be formed if the substance contains chlorine, bromine, or iodine, is then filtered off. The excess of silver present must then be thrown down with hydrochloric acid, and the sulphur and phosphorus in the clear filtrate estimated as baric sulphate and ammonic magnesic phosphate.

(5.) Other constituents remain as ash, and must be estimated in the usual manner.

VAPOR DENSITY.

Having determined by an ultimate analysis the exact chemical composition of a body, it is necessary (if the substance under examination be volatile) to determine the specific gravity of its vapor. We shall notice hereafter the important control that this determination exercises over the calculations derived from the ultimate analysis. We should here remark—

(α.) That with an organic, as with an inorganic compound, "its vapor density is one-half its molecular weight;" in other words, that the molecule of a compound body (no matter what number of atoms be present in the molecule) occupies in the state of gas twice the volume occupied by one atom of hydrogen (H=1) under like conditions of temperature and pressure. Thus a molecule of water gas (H_2O) occupies two volumes, or , the atom of hydrogen (H) occupying one volume, or .

(β.) It follows, if the molecule of a compound body in the state of vapor be twice the volume of an atom of hydrogen, that "*the specific gravity of any compound gas or vapor referred to hydrogen as unity, must be one-half its molecular weight.*" Thus—

The molecular weight of $H_2O=18$. This, we have seen, occupies 2 volumes, *i. e.*, twice the volume occupied by H;—

Therefore $\frac{18}{2} = 9$, the relative weight or vapor density of water gas, hydrogen being 1.

(γ.) But to this general law we find certain exceptions. These exceptions are probably more apparent than real, and may be explained by the circumstance that many bodies, when heated to their boiling point, decompose, so that the vapor experimented upon is not the pure vapor of the original body, but a mixture containing the vapors of the new compounds of decomposition. This form of decomposition is termed "*dissociation*" (*see* page 13). For example, a molecule of sulphuric acid (H_2SO_4), as a gas, is found to occupy not (as it should do) 2 volumes, but more than 2 volumes, the reason being that when sulphuric acid is heated above its boiling point, it is decomposed more or less completely into sulphuric anhydride and water

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($H_2SO_4 = H_2O + SO_3$). Hence, if we were determining its vapor density, our experiment would be conducted, not with pure sulphuric acid vapor, but with a vapor containing the mixed decomposition products, water and sulphuric anhydride.

It will be evident that if *dissociation was complete,* the molecule of a substance (such, *e. g.*, as H_2SO_4) would occupy, in a state of vapor, 4 volumes instead of 2 volumes; that is, the H_2O formed would occupy 2 volumes, and the SO_3 2 volumes. This being the case, the observed specific gravity would be one-fourth (and not one-half) the molecular weight, the molecule appearing to occupy 4 times the volume of a hydrogen atom. But *dissociation may be, and usually is, only partial,* commencing at, or a little above, the boiling point, and becoming more and more perfect as the temperature is increased.

The difficulty in determining vapor densities arising from dissociation, has been in some cases overcome by altering the relationship between the relative quantities of the products of dissociation, the tendency of compounds to combine being augmented by the presence of one of the compounds in excess. Thus, if we attempted to determine the vapor density of phosphoric chloride (PCl_5), we should find that it would split up into PCl_3 and Cl_2. If, however, we mix phosphorous chloride (PCl_3) with phosphoric chloride (PCl_5) the chlorine set free by heat from the PCl_5, being in the presence of a large excess of PCl_3, instantly combines with it to form PCl_5, enabling us at once to obtain the true vapor density of the phosphoric chloride Thus in some cases the difficulties arising from dissociation have been met.

We now proceed to consider *the determination of vapor densities.*

Determination of Vapor Densities.

This may be effected in one of two ways; either

I. By determining the weight of a given volume of vapor; or

II. By determining the volume of a given weight of the substance.

I.—*By determining the weight of a given volume of vapor* (process of Dumas).

(α.) Provide either a clean dry glass flask, or one of porcelain, if glass will not stand the necessary heat. The flask must have a long and finely drawn out neck, and be capable of holding from 200 to 300 c.c. Weigh the flask accurately, noting at the time the temperature and pressure.

Thus we learn the weight of the flask filled with air at a definite temperature and pressure.

(β.) Introduce now into the flask a quantity (say 50 to 100 grains) of the substance to be examined, and place the flask containing the compound in a water, oil, or mercury bath, the neck of the flask being

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external to the bath. The temperature of the bath employed must be considerably above the boiling-point of the body under examination. Hence the vapors of cadmium (860° C.), or of zinc (1040° C.), must be used if necessary. The vapor of the substance, as it is evolved, expels the air of the flask. When the evolution of vapor from the flask ceases, the neck of the flask is to be sealed, the temperature of the bath and the atmospheric pressure being noted at the time. When the flask is cold it is to be weighed, the temperature and pressure being again recorded.

Thus we learn the weight of the flask filled with the vapor of the substance under examination, at a definite temperature and pressure.

(γ.) The extreme point of the flask is now to be broken off under mercury. If the air of the flask has been entirely expelled, the mercury immediately rushes into, and completely fills the flask. By weighing the mercury that thus enters the flask, the capacity of the flask may be determined.

Thus we learn the capacity of the flask.

If, however, the mercury does not completely fill the flask, it proves that the expulsion of the air by the vapor was not complete. Under these circumstances, weigh *first* the mercury that enters the flask, and *secondly*, the total mercury required to fill the flask.

Thus, by the difference between these two weighings, we learn the quantity of residual air in the flask at the time of the experiment, whilst the weight of the mercury required to fill the flask, gives us the gross capacity of the flask.

Example (from Roscoe).—A volatile hydro-carbon (C_6H_{14}) is taken for the experiment. The barometric pressure is throughout taken at 760 mm.

Weight of the flask filled with air (temperature 15·5° C.)	= 23·449 grms.
Weight of the flask filled with the vapor of the hydro-carbon (temperature 110° C.)	= 23·720 grms.
Capacity of the flask	178 c.c.

From these data we enquire,—

(1.) *What bulk would* 178 c.c. *of air* at 15·5° C. (the temperature at which the flask containing air was weighed) *occupy at* 0° C. (the standard temperature, *see* p. 33)? Ans. 168·4 c.c.

(2.) *What is the weight of this volume of air?* Every c.c. of air at 0° C. and 760 mm. weighs 0·001293 grms. Therefore $0{\cdot}001293 \times 168{\cdot}4 = 0{\cdot}218$ grms., the weight of 168·4 c.c. of air at 0° C., and 760 mm. pressure; in other words the weight of the air the flask contains at 0° C.

(3.) The weight of the flask without air is therefore 23·231 grms. [23·449 grms. (flask + air) − 0·218 grm. (weight of air) = 23·231 grms. (weight of flask).]

(4.) The weight of the flask filled with vapor is 23·720 grms. If we subtract from this, the weight of the flask, we obtain the weight of the vapor in the flask [23·720 (flask + vapor) − 23·231 (weight of flask) = 0·489 grm. (the weight of the vapor).]

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(5.) 178 c.c. of hydrogen at 110° C. weighs 0·01134 grm. (1 c.c. of hydrogen at 0° C. and 760 mm. weighs 0·0008936 grm. (*see* page 35).

Therefore $\frac{0{\cdot}489}{0{\cdot}01134} = 43{\cdot}13$ { The density of the vapor of C_6H_{14} compared to hydrogen as unity.

In this example we have omitted such minor details as the expansion of the glass flask, the errors of the thermometer, etc. If the pressure varied during the experiment, due allowance must be made.

If the air be not wholly expelled from the flask by the vapor, the residual air must be deducted from the total capacity of the flask, and the calculation made on the result.

II.—The vapor density may also be estimated "by determining the volume of a given weight of the substance." (Process of Gay Lussac.)

A sealed glass bulb, containing a known weight of the substance to be examined, is introduced into a graduated tube full of, and standing over, mercury. The whole apparatus is then lowered into a bath of hot oil or other liquid, the heat of which bursts the glass bulb, and converts the whole of the volatile substance contained therein into vapor. The volume of vapor is then noted, and also the temperature of the bath, the atmospheric pressure, the height of the mercury in the graduated tube (the downward weight of which tends to *expand* the vapor), and the depth of the oil bath pressing on the mercury (the downward weight of which tends to *contract* the vapor). From these data, the vapor density may be calculated.

Hofmann's modification of the above process, consists in enclosing the graduated glass tube in a second and larger tube, through which currents of the vapor of water or other body can be passed. In this way the trouble of lowering the whole apparatus into the oil bath is avoided. The volume of the vapor, the temperature, the pressure, and the height of the mercury column must be noted. The weight of hydrogen, which under the same conditions would occupy a similar volume is then estimated, and

$$\frac{\text{the weight of substance examined}}{\text{the weight of hydrogen}} = \left\{ \begin{array}{l} \text{the vapor density} \\ \text{required.} \end{array} \right.$$

We have now to consider

The Application of the Facts deduced from the Ultimate Analysis, and from the Determination of the Vapor Densities of Organic Bodies.

(1.) *We learn firstly, the percentage composition of a body.* This, as we have noticed, is at once deduced from the analysis (page 370). Thus it was shown that every 100 parts of sugar contained—

Carbon, 41·98; hydrogen, 6·43; oxygen, 51·59.

(2.) From this percentage composition is deduced *the empirical formula* of the body, *i. e.*, the simplest possible expression of the rela-

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tive quantities of the several elements present. Thus the empirical formula for sugar is $C_{12}H_{22}O_{11}$. The rule for estimating the empirical formula from the percentage composition is as follows (*see page* 44):—"Divide the percentage numbers by their respective atomic weights, and divide these quotients by their greatest common divisor," thus—

	Percentage composition of sugar.		At. Wt. of element.		
Carbon.....	41·98	÷	12	=	350.
Hydrogen	6·43	÷	1	=	643.
Oxygen	51·59	÷	16	=	323.

The relationship between $C_{350}H_{643}O_{323}$ (dividing each by 30) is *very nearly* expressed by the formula $C_{12}H_{22}O_{11}$.

Very nearly, we say, but *not exactly*, for it has been already remarked (page 371) that slight experimental errors are inseparable from an ultimate analysis. This experimental error may be checked, amongst other methods mentioned under the determination of the molecular formula (page 379), by *reckoning back* the formula deduced to the percentage composition, as well as calculating the percentage composition into the formula. The question is—Do the errors fall, both as regards (1) *direction* and (2) *amount*, within the recognised experimental errors, remembering that as regards (1) *direction*, the carbon is commonly deficient and the hydrogen in excess, and that as regards (2) *amount*, the deficiency of the one or the excess of the other, should not exceed 0·2 or 0·3 per cent.?

Thus in the case of sugar—

I.	II.
From the percentage composition:—	From the formula $C_{12}H_{22}O_{11}$, we calculate the percentage composition as follows:—
Carbon .. .. 41·98	Carbon .. .. 42·11
Hydrogen .. .. 6·43	Hydrogen .. 6·43
Oxygen .. .. 51·59	Oxygen .. .. 51·46
we calculate the formula:—	
$C_{12}H_{22}O_{11}$	

This close correspondence of results proves the accuracy of the formula $C_{12}H_{22}O_{11}$.

(3). Our results, further, help us to determine the *molecular formula* of the body. By this we mean "*the atomic constitution of the molecule, which, converted into vapor, corresponds to the volume formed by* 2 *atoms of hydrogen* (hence called a 'two-volume formula') *under similar conditions of temperature and pressure.*" The advantage of the molecular over the empirical formula is, that it represents not only the number of parts by weight, but also a quantity which, as a gas, occupies a known volume (*viz.*, 2 volumes). Comparison is thus simplified.

(*a.*) *What is the relationship between the empirical and the molecular formula of a body?*

(1.) They may be identical;

(2.) If not identical, the molecular formula is always some simple multiple of the empirical formula. Thus—

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CH represents the empirical formula for benzene;
C_6H_6 ,, molecular ,, ,,

We next enquire—

(β.) *How is the molecular* (or *two-volume*) *formula determined?*

(1st.) By the actual determination, when possible, of the vapor density of the body. The vapor density of a body (that is, the relative weight of one volume) is always one-half its molecular weight, (that is, the actual weight of two volumes).

CH, we learn from its ultimate analysis, represents the simplest expression of the relative amounts of carbon and hydrogen in the liquid called benzene. From this formula we should estimate the vapor density of benzene as 6·5 thus—

$$CH = \frac{12 + 1}{2} = 6{\cdot}5;$$

Experiment, however, shows that the vapor density of benzene is 39 or 6·5 + 6. Hence C_6H_6 must be the molecular formula—

$$C_6H_6 = \frac{72 + 6}{2} = 39{\cdot}0$$

Or we may state the facts thus:—the parts by weight of benzene represented by the formula CH, when converted into vapor, only measure one-sixth of the volume produced by 2 unit weights of hydrogen; whilst the parts by weight represented by the formula C_6H_6, measure, when converted into vapor, the volume produced by 2 unit weights of hydrogen, under similar conditions of temperature and pressure. Hence C_6H_6 is regarded as the molecular formula for benzene.

(2ndly.) It is, however, not always possible to estimate the vapor density of a body, for it may be non-volatile, or it may decompose when heated. Hence other means must be adopted to determine the parts necessary to form two volumes, *if the substance could be volatilized unchanged.*

(α.) Such means consist, in *the analysis of the compounds it forms with well-known bodies*, in other words, its powers of combination and saturation.

(1.) In the case of organic acids or salt radicals, the silver or lead salt is commonly examined. For example, suppose we were determining the molecular formula of acetic acid. From the ultimate analysis we learn that CH_2O constitutes its empyrical formula. One atom of silver will replace (we know) one atom of the hydrogen of the acetic acid to form acetate of silver. By analysis we find that every 100 parts of this acetate of silver contains—

Silver	64·68 parts.
Carbon, Hydrogen and Oxygen	35·32 ,,

Hence the atoms of C, H and O, combined with 108 atoms of silver (108 being the atomic weight of silver), may be found by the equation—

$$64{\cdot}48 : 36{\cdot}32 :: 108 : x = 58{\cdot}98.$$

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To this 58·98 add 1 (=59·98), to allow for the hydrogen displaced by the silver. Hence the molecular weight of glacial acetic acid is 59·98, and its molecular formula (allowing for experimental error) must be $C_2H_4O_2$. Thus—

$$\begin{aligned} C_2 &= 24, \\ H_4 &= 4, \\ O_2 &= 32 = 60{\cdot}00, \text{ or } 59{\cdot}98 \text{ nearly.} \end{aligned}$$

(2.) In the case of organic bases, the neutral compounds formed with well-known mineral or organic acids, must be examined.

(β.) The study of the substitution products the body forms.

(γ.) The action of reagents.

(δ.) The calculation of the specific heat, and of the specific gravity of the body.

It is most important to bear in mind exactly what a molecular formula teaches, and what it does not teach :—

(α.) *It teaches* the actual chemical composition of a body, and its vapor density.

(β.) *It does not teach* the chemical formation of a body, nor its mode of decomposition ; nor does it help us in the least degree to distinguish between *isomeric* compounds (*see* page 48).

To supply these wants, *Rational, Constitutional or Structural Formulæ* are employed. A rational formula is designed to teach something of the nature and properties, and also of the formation and decomposition of a substance.

It will be, of course, understood that rational formulæ are purely *theoretical* formulæ, and merely represent probabilities. They are not to be regarded as *actual representations* of the constitution of a body, but merely as the best representations our present knowledge enables us to form.

One compound may possess many rational formulæ, and we use them according to the decomposition or reaction we desire to represent. Thus, acetic acid ($C_2H_4O_2$) has numerous rational formulæ, amongst which we may mention the following :—

(1.) $H(C_2H_3O_2)$: This implies that acetic acid is a *monobasic acid*, the one H placed on one side, implying that it may be replaced by a monovalent metal, or by a univalent alcohol radical. Thus we have the bodies—

$Ag'.C_2H_3O_2$	...	...	Argentic acetate.
$Ba''.(C_2H_3O_2)_2$	...	...	Baric acetate.
$(C_2H_5)'.(C_2H_3O_2)$	...	...	Ethyl acetate.

(2.) $C_2H_3O(HO)$: When phosphorus pentachloride acts on acetic acid, one of chlorine takes the place of one of the group (HO) (α.); and when the acetic chloride thus formed is acted on with water, one of the

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group (HO) takes the place of 1 of chlorine (β.), as will be seen in the following equations. This formula denotes, therefore, the displacement of HO by Cl.

(α.) $C_2H_3O.(HO)+PCl_5=C_2H_3O.Cl+HCl+POCl_3$.

(β.) $C_2H_3O.Cl+H_2O=C_2H_3O(HO)+HCl$.

(3.) $CH_3.CO_2.H$: This represents that on electrolysing acetic acid, hydrogen is given off at the — pole, and ethane (C_2H_6) and carbonic anhydride at the + pole ($2CH_3.CO_2.H=H_2+C_2H_6+2CO_2$).

(4.) $CH_3.CO.HO$: This formula represents the fact that the radical acetyl (C_2H_3O) consists of carbonyl and methyl. It shows how marsh gas (CH_4) is evolved when potassic acetate is heated with potassic hydrate, $CH_3.CO.KO+KHO=CH_4+(CO)''(KO)_2$. Also that acetic acid forms metallic salts, as potassic acetate ($CH_3.CO.KO$); also that by the action of PCl_5, the HO may be exchanged for Cl, etc.

PROXIMATE ANALYSIS OF ORGANIC BODIES.

By a proximate analysis is implied the separation of the *proximate principles* of bodies, as, *e. g.*, the separation of milk into fat, sugar, casein, etc. We can lay down no general rules for a proximate, as we are able to do for an ultimate analysis, each substance requiring special treatment.

The *microscope* and microscopic reactions, afford great aid in proximate analysis, enabling us to detect and to identify various bodies, such as, *e. g.*, *starch cells* by their appearance and reactions with iodine; *cellulin*, by its turning blue with iodine, after having been first moistened with dilute sulphuric acid; *woody tissue*, by its being darkened by sulphuric acid, and turning brown on being afterwards treated with iodine; *corky tissue*, by the absence of any change with sulphuric acid or with iodine, etc., etc. Further in separating crystallizable bodies, the microscope enables us to detect admixtures by the presence of crystals of different orders.

Dialysis, again, as a means of separating crystalloids from colloids, affords invaluable aid.

The following are the chief physical and chemical means adopted for separating the proximate principles of organic bodies.

1. *By spontaneous exudation*, as, *e. g.*, gums, resins, etc.
2. *By mechanical pressure*, as, *e. g.*, oils (linseed, castor, etc.).
3. *By the action of heat.*—This may be employed either—

(α.) To melt out resins and fats, or

(β.) To sublime the volatile acids (benzoic), or

(γ.) To distil the volatile oils, or

(δ.) To separate admixtures of volatile liquids by fractional distillation.

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4. *By the action of solvents*:—

(α.) *Water* { *cold*—to dissolve gums, sugar, certain coloring matters, etc.
boiling—to dissolve starch, salts, etc.

(β.) *Alcohol*—to dissolve volatile oils, resins, certain alkaloids, coloring matters, etc.

(γ.) *Ether, chloroform,* or *benzol*—to dissolve fixed oils, camphor, caoutchouc, certain alkaloids, etc.

(δ.) *Dilute acids and alkalies*—the use of which, however, is generally to be avoided, owing to the changes they induce in the organic body itself.

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CHAPTER XX.

THE NATURAL AND ARTIFICIAL CHANGES OF ORGANIC BODIES.

FERMENTATION — Varieties—I. Alcoholic—II. Lactic—III. Butyric—IV. Mucous—V. Acetous—Conditions necessary for Fermentation—Circumstances influencing Fermentation—Theories to account for it—Practical applications. PUTREFACTION—Disinfectants. EREMACAUSIS. Action of Heat—Action of Acids—Action of Alkalies—Action of Haloid Elements—Action of Nascent Oxygen and Hydrogen—and of other Reagents—Action of Light and Electricity.

The transformations which organic bodies undergo are twofold :—(A.) *Natural or Spontaneous*; and (B.) *Artificial.*

A.—NATURAL AND SPONTANEOUS.

It may be stated generally, that all organic substances are naturally prone to resolve themselves into simpler parts or groups. This resolution is effected in one of three ways :—

I. By fermentation.
II. By putrefaction.
III. By eremacausis or decay.

I. FERMENTATION.

Definition.—"A process whereby certain organic substances, under the influence of contact with a nitrogenous body called a ferment, are resolved into simpler groups." We may note that fermentation is accompanied by the development of certain minute living organisms, the existence of which may be either a *cause* or a *consequence* of the chemical change; that no offensive odors are evolved during the process; and that the products are most often of a useful nature.

We shall investigate the subject of fermentation in the following order :—

1. Its principal varieties.
2. The conditions necessary for its existence.
3. The conditions influencing its action.
4. The theories to account for it.
5. Its practical applications.

(1.) The Varieties of Fermentation.

There are five varieties of fermentative action, their distinctive names being derived from the principal product furnished :—

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(α.) *The alcoholic* or *vinous fermentation*, in which *alcohol* is formed.
(β.) *The lactic fermentation*, in which *lactic acid* is formed.
(γ.) *The butyric fermentation*, in which *butyric acid* is formed.
(δ.) *The mucous* or *viscous fermentation*, in which a gummy matter is formed.
(ε.) *The acetous fermentation*, in which acetic acid is formed.

(α.) **The Alcoholic or Vinous Fermentation:** *i.e.*, a fermentation characterised by the formation of alcohol. This results from the action of yeast on a solution of grape sugar, ethylic alcohol and carbonic anhydride being the chief products. The change of 95 per cent. of the sugar thus fermented may be represented as follows:—

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2.$$
Grape sugar = Ethylic alcohol + Carbonic anhydride.

But besides these, other products are formed from the remaining 5 per cent. of sugar; *viz.*, free hydrogen, the homologues of ethylic alcohol (as propylic alcohol, etc.), a hydrocarbon of the C_nH_{2n+2} series, glycerine (to the extent of 3 per cent. of the sugar fermented (Pasteur)), mannite, acetic acid, succinic acid (0·5 per cent.), etc. Many of these products are, however, no doubt the result of secondary action, either of the nascent hydrogen (as, *e.g.*, in the production of glycerine, mannite, etc.), or of the nascent oxygen (as, *e.g.*, in the production of succinic acid) resulting from the decomposition of water, which decomposition it is believed always occurs during the process.

The active agent of alcoholic fermentation is believed to be the cells of the *torula cerevisiæ*.

It is to be specially noted that cane-sugar and its isomerides (*i.e.*, the $C_{12}H_{22}O_{11}$ group) will not undergo vinous fermentation, this action being limited to grape-sugar and its isomerides (*i.e.*, the $C_6H_{12}O_6$ group). The change, however, of cane-sugar into grape-sugar, under the influence of a ferment, is rapid, the specific gravity of the liquid increasing as the change takes place, a solution of cane-sugar having a lower gravity than one containing an equivalent amount of grape-sugar.

(β.) **The Lactic Acid Fermentation;** *i.e.*, a fermentation characterised by the formation of lactic acid. This results from the action of putrefying cheese or milk on grape or milk-sugar. It is necessary, in order to neutralize the lactic acid as soon as formed, that the solution should contain either chalk (in which case a calcic lactate is produced), or zinc white (when a zincic lactate results), the presence of a trace of free acid entirely preventing the continuance of the fermentation by coagulating the casein and rendering it insoluble. This change into lactic acid may be represented as follows:—

(α.) $C_6H_{12}O_6$ (glucose) = $2C_3H_6O_3$ (lactic acid).
(β.) $C_{12}H_{22}O_{11}$ (lactose) + H_2O = $4C_3H_6O_3$ (lactic acid).

Mannite is also formed during the process. It is necessary that

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the lactates themselves should be removed from the action of the ferment as soon as possible, otherwise they are converted into butyrates. The lining membrane of the stomach of the calf (rennet) and animal membranes generally, are specially active in inducing this variety of fermentation. In the case of milk, the casein acts as the ferment on the milk-sugar. Hence milk contains both the ferment itself, and the body to ferment.

The active agent of the lactic acid fermentation is believed to be the *penicillium glaucum.*

(γ.) **The Butyric Fermentation,** *i.e.*, a fermentation characterized by the formation of butyric acid.

This results from *the prolonged action* of the lactic acid ferment on the lactic acid, whereby butyric acid (which by the action of chalk is converted into butyrate of lime) together with free hydrogen, carbonic anhydride, acetic and caproic acids, are formed. The butyric fermentation is in fact the advanced stage of the lactic acid fermentation. Thus :—

$$2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2.$$

Lactic acid = Butyric acid + Carbonic anhydride + Hydrogen.

The active agent of the butyric fermentation is believed to be the same as that of the lactic fermentation, viz., the *penicillium glaucum.*

(δ.) **The Mucous or Viscous Fermentation,** *i.e.*, a fermentation characterized by the formation of gummy matters. This results from the action of certain nitrogenous substances on sugar, a gum (arabin), mannite ($C_6H_{14}O_6$) a non-crystallizable sugar, and lactic acid, forming the products. This fermentation commonly results in fermenting the juice of the sugar beet. It sometimes occurs in sweet *white* wines that have been kept too long, the action being capable of arrest by the addition of a little alum or sulphurous acid to the wine. It does not occur in *red* wines, the astringent matter derived from the grape skins preventing them from becoming "ropy."

(ε.) **The Acetous Fermentation,** *i.e.*, a fermentation characterized by the formation of acetic acid.

This results from the action of the acetous ferment, (the *mycoderma aceti,*) on alcohol. The action does not take place with pure alcohol, or when the alcohol is simply mixed with water, its admixture with some changeable organic substance being an essential condition.

$$C_2H_6O + O_2 = C_2H_4O_2 + H_2O.$$

Alcohol + Oxygen = Acetic acid + Water.

This action, however, can scarcely be considered fermentation, but simply a process of oxidation (decay), the mycoderm acting (1) as a carrier of oxygen to the alcohol, and (2) as the means of bringing the oxygen and the alcohol into actual contact. This action is analogous to that which occurs in the oxidation of alcohol to aldehyde and to acetic acid by spongy platinum.

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The active agent, as we have said, of this change is the *mycoderma aceti*.

Thus it would appear that elementary plants have the power of breaking up organic bodies, each little organism having its own special soil on which to work, the products formed, being dependent both on the organism and on the soil.

(2.) The Conditions Necessary to Produce Fermentation.

(*a*). *The presence of a ferment;* that is of a nitrogenous albuminous body in a state of active decomposition. Illustrations of ferments are found in *Emulsin*, the active agent of the bitter almond in converting the amygdalin into hydrocyanic acid, &c.; in *Myrosin*, a ferment-like substance present in the seeds of the black and white mustard, which converts the myronate of potassium into the oil of mustard (C_3H_5CNS) together with glucose and hydric potassic sulphate; in *Diastase*, a body found in malt, saliva, &c., and by the action of which starch is converted into glucose; in *Casein*, which in milk induces lactic acid fermentation of the sugar; and, amongst many other illustrations that might be quoted, in *Yeast*, which is the ordinary ferment employed for setting up alcoholic fermentation.

This last ferment, the ordinary beer yeast, has been specially studied. When the yeast is merely dried at a low temperature, (forming what is called "dried yeast,") its power as a ferment is not impaired, but if the yeast be boiled in water it is then completely destroyed. "German dried yeast," consists of the dried yeast cells produced in the fermentation of rye for making Hollands.

Yeast, however, is a complicated ferment. It consists of two kinds of cells, (1) large round granular cells (torula cerevisiæ), and (2) certain oval-shaped cells of a much smaller size (penicillium glaucum). If the yeast be mixed with water, and then filtered through paper, the smaller cells pass through with the water, leaving the larger cells on the filter paper. It is found that *the large cells* generate vinous, and *the small cells* lactic fermentation, when they are added respectively to a solution of sugar.

When yeast is added *to a solution of pure sugar* it sets up fermentation, but the yeast-cells are for the most part destroyed as fermentation proceeds. A few fresh yeast-cells may be formed, but if so, it is at the expense of the materials produced by the disintegration of other yeast-cells. Hence, a given quantity of yeast can only convert a limited quantity of *pure* sugar into alcohol. When the yeast is added to a *solution of sugar*, the solution also containing *nitrogen* in some form or another, and *phosphates*, it then not only ferments the sugar, but propagates itself. Under such circumstances the addition of a little yeast, owing to its rapid growth, will convert an almost unlimited amount of sugar into alcohol. Thus the presence of nitrogen and

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phosphorus, in a combined form, are essential conditions for the growth and propagation of yeast-cells.*

In the case of grape-juice no ferment need be added, as, after exposure to the air for an hour, or even less, the vegetable albumen in the juice undergoes decay by oxidation, and acts as a ferment to the sugar.

It has been suggested that certain miasmas act as blood-ferments, and induce the diseases ordinarily known as zymotic (*ζύμη*, ferment) or ferment-diseases.

We have remarked that all ferments contain nitrogen. Nitrogen is an element remarkable for rendering the bodies in which it occurs unstable. The chemical relationships of nitrogen are worthy of note: it stands mid-way in the chemical scale between metals and metalloids, without any great affinity for either the one or the other. It combines both with oxygen and with hydrogen (and indeed with most bodies), but its *direct* union is not easily effected. Hence, its attractions being equally powerful in opposite directions, great instability invariably characterizes the compounds in which it is present.

(*β.*) *A body to ferment.* The sugars (glucoses) are, *par excellence*, the bodies peculiarly liable to ferment. If yeast be added to a solution of gum no action will be apparent, nor will the yeast itself be propagated. The action of yeast, however, is not confined to sugar; for if it be added to a solution of malic acid, succinic, acetic and carbonic acids are formed, although it is to be remarked that in this case the yeast itself does not propagate.

(*γ.*) *The actual contact of the ferment and the body to be fermented.*—The necessity for actual contact was proved by Mitscherlich as follows: A glass tube, the bottom of which consisted merely of a piece of fine filter-paper, was partially immersed in a solution of sugar. The solution rapidly penetrated the pores of the paper, and filled the tube to the level of the external liquid. A small quantity of yeast was then added to the liquid *in the tube*, when the solution contained in the tube, after a short time, commenced fermenting, but there were no signs of fermentation in the solution external to the tube, the piece of bibulous paper stopping the actual contact of the yeast-cells with the external fluid by stopping the passage of the yeast globules, although it did not interfere with the intercommunication of the liquids.

(*δ.*) *A certain temperature.* At 32° F. (0° C.) fermentation is arrested. From 32° F. to 68° F. (0° C. to 20° C.) it gradually increases in intensity with the rise of temperature. From 68° F. to 104° F. (20° C. to 40° C.) it is most active. At 120° F. (49° C.) the process is again stopped. Hence certain times of the year are preferable for brewing (especially the autumn), the temperature at such times falling within the proper limits.

* Yeast yields from 6 to 8 per cent. of ash, which consists entirely of alkaline and earthy phosphates. (Mitscherlich).

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(ε.) *The presence of moisture.* Water is necessary to bring the particles into contact. Dry yeast and dry sugar cannot ferment.

We may note, lastly, that *the presence of air* is not necessary for fermentation, provided the previous conditions be fulfilled.

It has nevertheless been proved by Pasteur, that the action of the air in the process of fermentation is not to be disregarded. For it may act either (1) as a carrier of the ferment germs, or (2) as an oxidiser, inducing the decay of certain nitrogenous bodies present in a solution, thereby rendering them capable of acting as ferments.

(1.) If a solution of sugar, no yeast having been added, be exposed to the atmosphere, it becomes loaded before long with the lower forms of organic life, and the solution begins to ferment. If, however, the air before being allowed to come into contact with the sugar solution, be passed either through a red-hot tube, or through a tube containing cotton-wool (care being taken that the saccharine liquid itself has been absolutely freed from germs by previous boiling), no fermentation will occur; but if the dust strained from the air by the cotton-wool be placed in the solution, rapid decomposition of the sugar results.

Hence Pasteur concludes that the air may act as the carrier of the seeds necessary to start fermentation in a solution disposed to ferment.

(2.) In the case of wine juice, which ferments spontaneously, the air is supposed to oxidise the vegetable albumen, which in a decomposed state is capable of acting as a ferment on the sugar.

(3.) The Circumstances Influencing Fermentation.

The following circumstances *prevent* fermentation:—

(α.) *The presence either of an excess of strong mineral acids, or of a trace of free alkali.*

(β.) *The presence of certain salts in the solution,* such as the sulphites, NaCl, $AgNO_3$, $CuSO_4$, etc.

(γ.) *The presence of certain alkaloids,* such as strychnia, quinia, etc. These do not, however, stop fermentation, if added *after* the process has commenced.

(δ.) *The presence of certain essential oils,* such as kreasote, turpentine, etc.

(ε.) *A solution containing more than one-fourth its weight of sugar.* The strength of the sugar solution is important. If it be *too strong,* fermentation is arrested, or rendered imperfect; if it be *too weak,* the action is slow and irregular.

(ζ.) *A solution containing more than* 20 *per cent. of alcohol.* Hence no fermented liquor can contain more than 20 per cent. of alcohol naturally. Anything in excess of this is evidence that spirit has been added (fortification) after the fermentation of the liquid was complete.

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Fermentation is influenced by many other causes. Thus—

(1.) *The products formed at different temperatures vary.* Thus, if yeast be made to act at a temperature of 70° F. (21·1° C.) on malic acid, it forms amongst other things succinic acid, whilst at a higher temperature it yields butyric acid.

(2.) *The alteration of pressure.* Fermentation is not stopped by placing the solution in a vacuum, but it is stated that under such circumstances the ratio of the alcohol to the carbonic anhydride formed, is different to that which occurs under ordinary atmospheric pressure, the CO_2 as well as the hydrogen, acetic acid, etc., becoming proportionately greater. (H. Brown.)

(4.) The Theories to Account for Fermentation.

We may note, *First*, that the ferment is destroyed during the fermentative process, the propagation and growth of new buds being due, partly to the disintegrated cells that have done their work, but principally to the nitrogenized matters and phosphates present in the solution. *Secondly:* that during the disintegration of the ferment cells, the body undergoing fermentation breaks up into simpler groups.

These being admitted facts, we may now notice the theories to account for the action of the ferment.

1. *Berzelius* explained it by the influence of a force which he called *Catalysis*, a word signifying Fermentation. He thus assumed the existence of a new force, but at the same time acknowledged indirectly his inability to perceive, or to detect the force, and the impossibility of explaining its action.

2. *Pasteur's* theory is as follows. The ferment, he considers, grows and multiplies at the expense of the sugar. This act of the ferment in withdrawing from the sugar a portion of its constituent matter, he regards as essential to the process of fermentation, and the primary cause of the sugar itself breaking up into simpler groups.

3. *Liebig* admits that the ferment may multiply at the expense of the sugar, but at the same time refuses to admit that the withdrawal of the matter from the sugar necessary for the propagation of the yeast cells, is the cause of the phenomena of fermentation. He considers that fermentation is due to the active state of change going on within the yeast cell, being communicated to the sugar in actual contact with it, thereby inducing in the sugar the breaking up process that the yeast cell itself is undergoing; in other words, that the disturbance going on in the yeast is mechanically communicated to the sugar, thereby effecting its breaking up and re-arrangement. Hence, according to Liebig, if the yeast grows at the expense of the sugar, it is merely to maintain a supply of the material necessary to keep it in a continuous state of disturbance.

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This theory is not unphilosophical although it is theoretical. That one body in motion may communicate its motion to another body not in motion, thereby overturning the existing equilibrium of that body, is a phenomenon of constant occurrence.

(5.) The Practical Applications of the Process of Fermentation.

(a.) *Alcoholic Fermentation.* (1.) *Wine-making.* The expressed grape-juice (the must) is first of all freely exposed to the air. The air decomposes the vegetable albumen of the juice, and this at once acts as a ferment on the grape sugar. If the sugar be in excess and the albumen deficient, we obtain *a sweet wine;* if the sugar be deficient, and the albumen in excess, *a dry wine* results. During fermentation, *argol* (acid potassic tartrate) is deposited, owing to its insolubility in dilute spirit. This circumstance constitutes the superiority of the grape over all other fruits for wine-making—the separation of the acids of other fruits, such as of gooseberries and currants (viz., malic and citric acids) not being effected during fermentation, and their taste consequently requiring to be masked by the addition of an excess of sugar.

The colour of red wines is derived from the grape skins. Effervescent wines are bottled before fermentation is complete.

(2.) In *brewing*—the barley has first to be malted. *Malting* consists in setting up germination, by the combined action of air, heat, and moisture on the seed, and then stopping germination by drying the seed at 140° F. (60° C.). The object of this is to convert (by oxidation) the gluten of the seed into *Diastase* (διάστασις decomposition) a peculiar, ferment-like body which has the power of changing the *insoluble* starch of the seed first into dextrin, and finally into *soluble* grape sugar. In nature, this process is necessary in order to supply the germ with its first food, which must be presented to it in a soluble form. The malt is then bruised, treated with water, and the liquid set aside for some time—any unconverted starch in the malt being thus brought into contact with the diastase, and its complete conversion into sugar effected. One part of diastase will convert 2,000 parts of starch into grape sugar, but the power of the diastase is itself exhausted during the process. The malt-mash is now strained, the clear liquor constituting what is called "the wort," and the undissolved portion "brewer's grains." The clear liquor is now boiled with hops, the bitter resinous principle of which (lupuline) not only gives flavour to the beer, but prevents it undergoing acetous fermentation. It is finally mixed with yeast, when the beer "works," that is "ferments," the sugar splitting up into alcohol and carbonic acid.

The malt used in the manufacture of porter is partially caramelized or "high dried."

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(3.) In *spirit-making*, the distiller prepares a wort or "*wash*," like the brewer, with this exception, that he mixes 4 parts of unmalted with 1 part of malted grain, the diastase of the latter being sufficient to convert the whole of the starch of the former into sugar. Thus, much of the labour and expense of malting is avoided. Moreover the distiller has no need to add hops to his wort, nor to consider the details of fermentation as the brewer is compelled to do, except that it should be as complete as possible. A large quantity of spirit is prepared from potatoes and also from corn, the starch of which may be converted into sugar by admixture with a little malt. In both cases, however, a small quantity of a very acrid oil (*fusel oil*) accompanies the ethylic alcohol, and this it is the duty of the rectifier to separate by careful distillation, the fusel oil being less volatile than the alcohol.

(4.) *In bread-making*, a little yeast is mixed with the dough, the object being to render the bread light and spongy. The sugar of the flour ferments, generates carbonic anhydride, which causes the bread to "rise," the spirit formed during "the working," escaping when the bread is baked.

Ammonic carbonate, sodic carbonate and hydrochloric acid, and lastly a stream of pure carbonic acid (Dauglish), have been suggested in bread-making in the place of yeast. In ancient days, a piece of dough in a state of incipient putrefaction (leaven) was used as a ferment, respecting which it was known that "a little leaven leaveneth the whole lump."

(β.) *The lactic fermentation.*—This is seen in the ordinary decomposition of milk into curds and whey. *Koumiss* is fermented mare's milk. It is a spirituous liquor.

(γ.) *The acetous fermentation.*—Illustrations of "acetification" may be noticed in beer turning sour, the acidity of which is due to acetic acid; and also in what is called the "quick vinegar process." This latter consists in allowing a heated mixture of alcohol and yeast (the yeast being added to supply the necessary nitrogenous matter) to trickle over wood shavings soaked in vinegar, the wood shavings serving as points of attachment for the mycoderm. It is essential that the supply of air be very free. If the supply of air be *limited*, aldehyde is formed, and much loss of vinegar results:—

C_2H_6O	+	O	=	C_2H_4O	+	H_2O.
Alcohol	+	Oxygen	=	Aldehyde	+	Water.

but if the supply of air be *free*, aldehyde is not formed, or if it be formed, is immediately oxidised:—

C_2H_6O	+	O_2	=	$C_2H_4O_2$	+	H_2O.
Alcohol	+	Oxygen	=	Acetic acid	+	Water.

The *French wine-vinegar* is prepared from light wines, by first mixing them with a little boiling vinegar, and then allowing the mixture to trickle over wood shavings into casks.

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The *English malt vinegar* is prepared from an infusion of malt, which is allowed to undergo both the alcoholic and the acetous fermentation. Commercial vinegar may by law contain the thousandth part of its volume of sulphuric acid, for the purpose of preventing its turning mouldy.

II. PUTREFACTION.

Definition.—A spontaneous change common to all nitrogenised organic bodies when exposed to the air, whereby they are resolved into new and simpler products. The action is accompanied by the evolution of unpleasant gases, which are for the most part compounds of sulphur and phosphorus.

It *differs from fermentation*, in that *unpleasant* products are evolved, as, *e.g.*, in the decomposition of a dead body. Moreover, a putrescible body is always a nitrogenised body, which at a certain temperature in contact with air and moisture, decomposes, and then becomes capable of acting as a ferment.

It *differs from eremacausis* or *decay* in that it is not oxidation, although air is necessary in the first instance to start the action. Modern investigations lead us to believe that the air may be the carrier of spores or ova, having the power of inducing the change. This is assumed because a body liable to putrefaction, does not putrefy if it be boiled in a flask, and when boiling, the neck of the flask plugged with cotton-wool. Nevertheless, we see *a relationship between eremacausis, putrefaction and fermentation.* Putrefaction is commenced, like decay or eremacausis, by the action of the air, whilst the putrescent body is capable of inducing fermentation in fermentable solutions. Moreover, like fermentation, putrefaction is always accompanied by the development of certain minute living organisms, fungi and infusoria.

(1.) The Conditions Necessary for Putrefaction.

(α.) *Air.*—The presence of air is essential only at the commencement of the process, and not when putrefaction has fairly commenced. Its progress is then independent of any aid external to itself. Thus fruits and meats are preserved in sealed air-tight tins.

(β.) *Moisture.*—A perfectly dry body does not putrefy. Thus vegetables when perfectly dry may be preserved for a considerable time (Masson's patent). The preservative action of sugar and salt has been ascribed by some to their attraction for moisture, and their power of withdrawing it from the putrescible body.

(γ.) *A temperature between* 40° *and* 200° F. (4·5° *and* 93·5° C.). Cold prevents putrefaction by increasing cohesion. Thus fish are preserved in ice. The stories of bodies of men and animals having been preserved in the ice of polar regions for many years are numberless. Warmth destroys cohesion, and thus aids putrefaction, whilst too great a heat destroys the body by burning it up.

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(2.) Means of Preventing Putrefaction.

By the general term "disinfectant" we include antiseptics and deodorizers.

An *antiseptic* is an agent that prevents putrefaction, and entirely stops the evolution of offensive gases.

A *deodorizer* is an agent that either absorbs or destroys the offensive gases after they are formed, but does not prevent their formation—in other words, does not prevent putrefaction.

Disinfectants are of two kinds—*natural* and *artificial*.

1. *Natural disinfectants*—

(α.) The *Atmosphere*. This acts both mechanically by its power of removing foul vapors and other matters, and chemically by effecting their oxidation.

(β.) *Water*. Its action is chiefly *mechanical*. In a river, during its flow, the organic matter becomes disintegrated, and rapid self-purification results. Every shower of rain purifies the air. Besides its cleansing powers, by reason of its endosmic action, water is inimical to the corpuscular structures of many specific contagia, for, by bursting their cell-like envelopes, it destroys their vitality.

(γ.) *Soil*. The power of soil is manifested in our graveyards. Owing to its porosity it effects the oxidation of decomposing matter. In the presence of alkalies, ammonia is rapidly oxidized to water and to nitric acid, whilst the ferric oxide present acts as a purveyor of atmospheric oxygen.

(δ.) *Light*.

(ε.) *Heat and Cold*. Vaccine matter loses its power at 140° F. (60° C.), and the virus of scarlet fever at 204° F. (95·5° C.). The common vibrio is destroyed at 300° F. (149° C.), and the black vibrio at 400° F. (204·5° C.). Others assert that none of the lower organisms will bear a temperature of 266° F. (130° C.) in air, or of 230° F. (110° C.) in water. [NOTE. A heat of 250° F. (121° C.), aided by a jet of steam, may be safely used in disinfecting textile fabrics.]

2. *Artificial disinfectants*.

(α.) *Mineral acids*, such as sulphurous, nitric, hydrochloric, sulphuric, and chromic acids. In this order, they have the power of stopping the development of infusoria in organic solutions, sulphurous acid being the least, and chromic acid the most powerful.

(β.) *Organic acids*, such as carbolic, cresylic, acetic, picric, benzoic acids; benzoic being the most powerful, and acetic the least so.

(γ.) *Alkalies*. Lime, potash, soda, and ammonia are only active disinfectants when they are used in a concentrated form. The use of lime in stables is for the purpose of assisting the oxidation of the organic matter. Added to sewage it kills infusoria and checks decomposition.

(δ.) The *haloids*. Iodine acts as a mild disinfectant, and chlorine

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as a powerful one; chloride of soda ("Labarraque's Liquid"); chloride of zinc ("Sir Wm. Burnett's Fluid"), the action of which is due to its power of coagulating albumen and of absorbing ammonia and sulphuretted hydrogen, chloride of aluminium ("chloralum"), which is neither an aërial disinfectant, nor has it the slightest deodorising power, and common salt and other chlorides are also frequently used.

(ϵ.) *Mineral Sulphates.* Sulphates of zinc, of iron ("Mudie's Disinfectant"), of alumina and of copper act as disinfectants, owing to their power of coagulating and destroying living organisms, and neutralizing offensive miasms.

(ζ.) *Potassic Permanganate* and *Chlorozone.*—These destroy *dead* organic matter, but have very little action, so far as we know, on *living* organic matter.

(η.) *Volatile Oils.*—Camphor, turpentine, etc. These hinder the development of fungi and animalcules, and generate ozone (?) It was believed in former times that the planting aromatic herbs about a house warded off pestilence.

(θ.) *Charcoal and other porous bodies.*—The action of such bodies is due to their power of absorbing noxious gases, and so bringing them into contact with condensed atmospheric oxygen, thereby effecting their destruction. But it must be remembered that it is essential for the action of charcoal, that there should be a free supply of atmospheric air.

Note, as regards disinfectants, the following practical hints:—

1. Certain disinfectants, such as chlorine, chloride of lime, sulphurous acid, carbolic acid, and volatile oils, are *aerial* disinfectants, and may be used for the purification of air; whilst others, such as chloralum, permanganate of potash, chlorozone, the mineral sulphates, chloride of zinc, etc., are useless for the purpose of purifying the air of a sick room, inasmuch as they are not volatile.

2. Neither chlorine, hypochlorous acid, carbolic acid, or sulphurous acid can be used to disinfect a chamber when a person is living in it, the quantity of the gas required to effect this object rendering the atmosphere absolutely irrespirable. Hence perfect disinfection is only possible when a room is vacated. The combustion of $1\frac{1}{2}$ ozs. of sulphur to every 100 cubic feet of space in a room, is necessary to effect complete disinfection.

3. Chloride of zinc and strong carbolic acid being corrosive bodies, should not be used for the disinfection of textile fabrics, but only for such purposes as the disinfection of fæcal matter, etc.

4. In disinfecting clothing *at the sick house*, boil the articles in water and then steep them in a solution of carbolic acid (℥iv. to 1 gallon.) To disinfect clothes completely, however, they must be submitted first to sulphurous acid, and then to a temperature for at least 6 hours of from 240° to 250° F. (115·5° to 121° C).

5. In disinfecting stables, cattle lairs, slaughter-houses, etc., there is nothing better than lime, on account of its detergent, as well as its disinfecting properties.

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6. In the treatment of sewage, lime and alumina act as excellent defæcatory and precipitating agents.

III. EREMACAUSIS (ἤρεμος gentle, καῦσις combustion) *Decay.*

Definition.—The decomposition of moist organic bodies *by oxidation* into simpler groups, or, in other words, the *slow burning* of organic bodies. This action is unaccompanied by any sensible elevation of temperature. It is seen in the *decay of wood*, when a brown powder (ulmin or humus) is left, the hydrogen oxidizing before the carbon; also in *the drying of oils*, the solidification being attended with the absorption of oxygen (which has been known to be so rapid that combustion has resulted); also in *the formation of acetic acid* from alcohol, and in many other processes.

(1.) The Conditions Necessary for Decay.

(α.) *The free access of atmospheric air.*—There are reasons to believe that the active agent in inducing eremacausis is ozone (see page 62). Thus bodies are found to be specially prone to decay after a thunderstorm, during which ozone is largely developed. Ozone, however, never accumulates in the air, but is used up as fast as formed to oxidize organic matter and vapours of organic origin. It is however more than probable that ordinary oxygen can carry on the process of decay when once the action has been started—although it must be remembered that the development of ozone itself, is a consequence or result of eremacausis, the decaying body furnishing the active agent necessary for its further destruction.

(β.) *The presence of moisture.*—Perfect dryness suspends decay, as it does fermentation and putrefaction. A body which is incapable of absorbing oxygen when dry, will often do so when moist. Thus in the "grass bleaching" of calicoes, where oxidation (eremacausis) only is relied upon for effecting the destruction of the coloring matters (a part of the cotton itself being oxidized at the same time), it is found to be essential to keep the fabrics moistened with water.

Thus again, in the formation of coal and peat, the presence of moisture is an essential condition.

(γ.) *A certain temperature.*—Cold by increasing cohesion interferes with decay; at the freezing point 32° F. (0° C.) decay is arrested. Warmth by its opposite effect promotes decay.

(2.) The Circumstances Influencing Eremacausis.

(α.) The action *is promoted by warmth.*

(β.) The action *is promoted by the presence of alkalies.* Thus in the formation of nitres the oxidation of ammonia takes place in the presence of a powerful base (*see* page 274); or again, in estimating

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the quantity of oxygen present in a mixed gas, its absorption may be effected by a mixture of pyrogallic acid and potassic hydrate (*see* page 98).

(γ.) The action *is checked by certain antiseptic salts.*

(δ.) The action *is promoted by the contact of an eremacausing body.* Just as one body on fire is capable of inflaming a body not on fire, so a body undergoing decay can by contact, produce decay in a substance liable to it. To prevent this contact oranges are packed in paper, etc., etc.

(ϵ.) The action *is promoted by the presence of porous substances such as charcoal,* etc., whereby the oxygen is absorbed and condensed, and its actual contact with the body effected.

(ζ.) The action is promoted by *an excess* of ozone in the atmosphere, such as occurs under certain atmospheric conditions.

(B.) ARTIFICIAL DECOMPOSITION.

I. Action of Heat on Organic Bodies.

Heat decomposes *all organic matter,* whereby new products (called the *products of destructive distillation*) are formed. These, on cooling, never resolve themselves into the same states of combination in which they existed originally in the organic body. The more complicated the organic body, the more easily is it decomposed by heat.

Heat acts *on many inorganic* compounds; sometimes these products do not re-combine on cooling, but most often the action of the heat is reversed by cold. For example, calcic hydrate by heat is resolved into lime (CaO) and water, but these in the cold combine to form calcic hydrate.

Heated *in the open air,* some organic bodies sublime, as, *e.g.*, benzoic acid ; others partially decompose, as for example in the formation of pyrogallic acid ($C_6H_6O_3$) and carbonic anhydride, from gallic acid ($C_7H_6O_5$); others simply burn, their carbon forming carbonic acid, and their hydrogen water, by combining either with their own oxygen or with the oxygen of the air.

When organic bodies are heated *in closed vessels,* the process is known as "destructive distillation." Simpler and more stable compounds are thus formed, and a residue of carbon mixed with the incombustible ash remains in the retort.

The products of destructive distillation vary with the body operated on, and with the temperature employed:—

(1.) This may be noticed, for example, *in the distillation of non-nitrogenised bodies, such as wood:—*

(α.) *At the lowest temperature,* compounds are given off containing much oxygen, such as water, acetic acid, carbonic anhydride, etc.

(β.) *At a higher temperature,* the compounds evolved contain less oxygen, such as carbonic oxide, wood spirit, kreasote, etc.

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(γ.) *At a still higher temperature,* various hydrocarbons distil over, such as toluene, xylene, and the different forms of paraffin, etc.; whilst

(δ.) *At a temperature approaching redness,* pure hydrogen predominates.

Products of the Action of Heat on Coal.

COMPOUNDS, Etc.	Formula.	Molecular Weight.	Specific Gravity.	Specific Gravity of Gas or Vapor.	Boiling point.		Fusing point.	
					° F.	° C.	° F.	° C.
Coal Gas.								
Marsh gas (Methane)	CH_4	16		0·559				
Olefiant gas (Ethene)	C_2H_4	28						
Acetylene (Ethine)	C_2H_2	26		0·92				
Hydrogen	H	1		0·0693				
Carbonic oxide	CO	28		0·973				
Nitrogen	N	14						
Vapors of vol. liquid hydrocarbons								
Vapors of carbon disulphide	CS_2	76	1·272	2·67	109·4	43		
Sulphuretted hydrogen	H_2S	34		1·171				
Carbonic acid	CO_2	46		1·524				
Tar and volatile oils								
Ammonia	NH_3	17						
Ammonia Water.								
Ammonic carbonate								
„ sulphide								
„ cyanide								
„ sulphocyanide								
Coal Tar.								
Neutral hydrocarbons.								
Liquid.								
Benzene	C_6H_6	78	0·85	2·77	177	80·6	40	4·45
Toluene	C_7H_8	92	0·881	0·87	230	110		
Xylene	C_8H_{10}			0·87	284			
Cumene	C_9H_{12}			0·85	338			
Solid.								
Naphthalene	$C_{10}H_8$	128	1·153	4·528	413·6	212	174	79
Anthracene	$C_{14}H_{10}$	178	1·147	6·741	680	360	416	213
Chrysene	$C_{18}H_{12}$	228					450	232
Pyrene	$C_{16}H_{10}$	202					350	177
Alkaline products.								
Ammonia	NH_3	17						
Aniline	C_6H_7N	93	1·02	3·21	360	182		
Picoline	C_6H_7N	93	0·961	3·29	271	135		
Quinoline	C_9H_7N	129	1·081	4·519	462	239		
Pyridine	C_5H_5N	79	0·986	2·92	242	117		
Acid products.								
Carbolic acid	C_6H_6O	94	1·065		370	187	95	35
Cresylic acid	C_7H_8O	108			397			
Rosolic acid	$C_{23}H_{22}O_4$							
Brunolic acid								
Acetic acid	$C_2H_4O_2$	60	1·06		243	117		

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(2.) *In the case of nitrogenised bodies, such as coal,* a part of the nitrogen is evolved as ammonia and basic bodies allied to it, such as aniline (C_6H_7N), quinoline, pyridine, etc., and also as cyanogen; whilst a part remains in the still, together with the carbonaceous residue.

It will be convenient here to notice the products of the destructive distillation of *Coal* and of *Wood*, the former serving as an illustration of the action of heat on a nitrogenized body, and the latter on a non-nitrogenized body.

(1.) The Products of the Distillation of Coal (or other nitrogenized substances).

The coal is distilled in retorts, connected with which are iron delivery pipes. These ascend perpendicularly for a few feet, and then curving round, dip below the liquid contents of a large horizontal pipe, called "the hydraulic main," which acts both as a water valve, and also as a receiver for the delivery pipes from numerous retorts. This pipe receives the tar and the gas liquor, through which the impure gas bubbles. Thus we obtain the coke in the retort, and the gas, the gas-water, and the coal tar, as the products of the distillation.

1. Coal Gas.—[A ton of coal yields from 9000 to 9500 cubic feet of gas.]

This is, as the table shows, a compound of a variety of gases and vapors. The relative proportion of the constituents is influenced greatly by the temperature at which the gas is prepared. The heat should always be at its maximum at the commencement of the operation. (α.) If it be *too high*, the heat of the retort decomposes the marsh and olefiant gases and the hydrocarbon vapors, carbon being deposited in the retort (gas carbon). An excess of hydrogen therefore escapes, and the illuminating power of the gas suffers in consequence. Hence the use of *exhausters* in order to hasten the exit of the gas from the retorts. Moreover, at a high temperature bisulphide of carbon is formed, the complete removal of which from the gas is practically impossible. (β.) If the heat *be too low*, the gas contains too great an excess of solid and liquid hydrocarbons, which tend to block up the tubes. These facts are well shown in a table (from Bloxam), illustrating the composition of coal gas at different periods of its distillation.

In 100 volumes.	1st hour.	5th hour.	10th hour.
Olefiant gas and volatile hydrocarbons ..	13·0	7·0	0·0
Marsh gas	82·5	56·0	20·0
Carbonic oxide	3·2	11·0	10·0
Hydrogen	0·0	21·3	60·0
Nitrogen	1·3	4·7	10·0

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The increase of the carbonic oxide at the fifth hour, may arise from the carbon decomposing the H_2O, and the increase of the nitrogen from the decomposition of the ammonia at high temperatures.

The gas as it leaves the hydraulic main needs *purification*. This is effected by various means :—

(1.) *The Condensers* (or *refrigerators*) consist of a series of bent iron pipes through which the gas is made to travel. By thus exposing a large surface of the gas to the air, any tar and ammonia liquor that escapes the hydraulic main, owing to the gas being superheated, is condensed.

(2.) *The Scrubber.*—This is a tower filled with wet coke. By this means the removal of the chief part of the ammonia from the gas may be effected. [The evil of the scrubber is that it diminishes the illuminating power of the gas, by removing at the same time as the ammonia, a portion of the more condensable hydrocarbons.]

(3.) *The Purifiers.*—The object of these is to remove the carbonic anhydride, (which is said to decrease the illuminating power of the gas,) and also the sulphuretted hydrogen, and other sulphur impurities in the gas, of which CS_2 is one.

To get rid of carbonic acid and sulphuretted hydrogen, (and also of the sulphocyanogen, cyanogen, etc.,) purifiers are constructed containing either—

(α.) *Lime*, a carbonate and a sulphide of lime being formed, or,

(β.) *Oxide of iron* (Fe_2O_3) (mixed with sawdust to prevent caking). The oxide removes sulphuretted hydrogen and hydrocyanic acid only from the gas. Thus, $Fe_2O_3 + 3H_2S = 2FeS + S + 3H_2O$.

With hydrocyanic acid, Prussian blue or some similar compound is formed.

The great advantage of oxide, is the ease with which the iron sulphide can be again converted into oxide by mere exposure to air (revivified), no nuisance being caused by the operation. The oxide may be used over and over again, the sulphur collecting in the mass until finally, after repeated revivifications, the percentage of sulphur present renders it of commercial value for the manufacture of oil of vitriol (*see* page 152).

To get rid of the sulphur impurities other than sulphuretted hydrogen, many processes have been suggested, of which the following are the most important, although all have proved more or less unsuccessful :—

(α.) *Sulphide of lime*, the evil of which is the nuisance occasioned by its use.

(β.) *By washing with the ammoniacal liquor.*

(γ.) *By steam at a high temperature*, whereby CO_2 and H_2S are formed, both of which are easily removed from the gas.

CS_2	+	$2H_2O$	=	CO_2	+	$2H_2S$.
Carbonic disulphide	+	Water	=	Carbonic anhydride	+	Sulphuretted hydrogen.

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(δ.) *By Red-hot lime.*

CS_2	+	$3CaO$	=	$CaCO_3$	+	$2CaS$.
Carbonic disulphide	+	Lime	=	Calcic carbonate	+	Calcic sulphide.

(ε.) *By a solution of lead oxide in caustic soda.*

CS_2	+	$2PbO$	+	$2NaHO$	=	$2PbS$	+	Na_2CO_3	+	H_2O.
Carbonic disulphide	+	Lead oxide	+	Sodic hydrate	=	Plumbic sulphide	+	Sodic carbonate	+	Water.

Finally the gas passes to the gasometer.

2. The Gas Liquor.—From this liquor, which contains numerous ammoniacal salts, but chiefly the carbonate, sulphide, cyanide and sulpho-cyanide, the various salts of ammonia in commerce are obtained, either by the direct action of acids on the liquor, or by setting free the ammonia by its distillation with lime (*see* page 311).

3. The Coal Tar.—This is distilled in iron retorts.

The tar contains three sets of products: (α) *those volatile at a low temperature;* (β) *those volatile at a high temperature;* (γ) *those not volatile at any temperature.*

(α.) *Those volatile at a low temperature.*—That which in the first instance distils over with the steam is called *light oil,* from its having a less specific gravity than, and consequently floating on, the condensed water. Every 100 parts of tar should yield 10 per cent. of light oil.

The light oil contains benzene, toluene, xylene, cymene, etc., contaminated more or less with dead oil. The light oil is again distilled, the distillate forming what is called *coal naphtha,* a quantity of heavy oil remaining in the retort. The coal naphtha is purified by shaking it up, first with sulphuric acid, whereby basic substances are removed, then with a dilute solution of potash to separate the carbolic acid, and finally with water. When decanted from the water it forms "rectified coal naphtha." This is now separated into its various constituents by fractional distillation:—

From 175°	to 180° F.	(79·4°	to 82·2° C.)	it yields	pure	benzene.
,, 180°	,, 230° F.	(82·2°	,, 110° C.)	,,	,,	?
,, 230°	,, 235° F.	(110°	,, 113° C.)	,,	,,	toluene.
,, 284°	,, 293° F.	(140°	,, 145° C.)	,,	,,	xylene.
,, 336°	,, 342° F.	(168·9°	,, 172° C.)	,,	,,	cymene.

Commercially, however, that portion which distils over between 175° and 250° F. (79·5° and 121·1° C.), is designated and sold as benzol or benzene.

(β.) *Those volatile at a high temperature.*—This constitutes the "dead oil." It is also called "yellow oil," from its peculiar color, and "heavy oil," from its being heavier than, and therefore sinking in, water. The last portions that distil over become nearly solid on cooling. Every 100 parts of tar yield about 25 per cent. of dead oil.

Dead oil contains carbolic acid, naphthaline, anthracene, aniline, quinoline, etc.

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Amongst the *first* products of the distillation of dead oil, is *carbolic acid* (C_6H_6O), the principal acid product of the oil. It comes over chiefly between 300° and 400° F. (149° and 205° C.). Upon its presence depends the antiseptic properties of the dead oil, which is largely used for preventing the decay of wood.

Amongst the *last* products of the distillation is *anthracene* ($C_{14}H_{10}$), a body of great commercial value in the manufacture of artificial alizarine. The first portion of the anthracene that distils over, is mixed with naphthalene ($C_{10}H_8$), and the last part with chrysene ($C_{18}H_{12}$). It is purified in the first instance by re-distillation, the first and the last portions being rejected. The intermediate portion is purified by crystallising either from a solution in alcohol, or in coal oils boiling between 212° and 248° F. (100° and 120° C.).

(γ.) *Those not volatile at any temperature.*—This constitutes the black residue in the retort called *pitch*. It is used in the preparation of Brunswick black, for asphalting, etc.

By the action of heat on horny matters, similar products to those already described are formed, the ammonia (hartshorn) being produced in great quantity, owing to the richness of horn in nitrogen.

(2.) The Products of the Distillation of Wood (or other non-nitrogenized substances.)

The following exhibits the difference in the chemical composition of coal and wood:—

Per 100 parts.	Carbon.	Hydrogen.	Nitrogen.	Oxygen.
Bituminous coal	79·5	5·5	1·9	13·1
Wood (dried oak)	51·6	5·7	0·2	42·5

We note therefore:—

(1.) That in wood there is about one-third less carbon than in coal.

(2.) That in wood there is a mere trace of nitrogen (0·2 per cent.), whilst in coal the quantity of nitrogen is considerable (1·9 per cent.)

(3.) That in wood there is more than three times as much oxygen as there is in coal.

(4.) That the proportion of hydrogen in both are about the same.

From this we should expect in the destructive distillation of wood:—

(1.) That the gases evolved from wood would be less illuminating than those from coal.

(2.) That there would be scarcely any nitrogenized products such as ammonia, etc., produced; but

(3.) That there would be a great excess of oxidized products, such as water, carbonic acid and oxide, acetic acid, etc.

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The wood contained in an iron cage, is placed in a retort and heated. Wood charcoal remains in the retort, and the products of the distillation are as follows:—

Wood Tar.

Solids.

Paraffin	C_nH_{2n+2}	Pyrene	$C_{16}H_{10}$
Naphthaline	$C_{10}H_8$	Chrysene	$C_{18}H_{12}$
Cedriret		Resin	
Pittacal			

Liquids.

Toluene	C_7H_8	Pyroligneous or acetic acid ..	$C_2H_4O_2$
Xylene..	C_8H_{10}	Wood naphtha ..	CH_4O
Cymene	$C_{10}H_{14}$	Acetate of methyl..	$CH_3.C_2H_3O_2$
Kreasote	C_7H_8O	Formate of methyl	$CH_3.CHO_2$
Picamar		Acetone	C_3H_6O
Kapnomor	$C_{10}H_{11}O$	Water	
Eupione	C_5H_{12}		

Gases.

Marsh gas	CH_4
Carbonic oxide	CO
Carbonic acid	CO_2

The distillate consists of water, tar, and naphtha.

The crude naphtha yields acetone (C_3H_6O), pyroligneous acid ($C_2H_4O_2$), and wood naphtha or methylic alcohol (CH_4O), this latter product being rectified by distillation below 212° F. (100° C.).

Paraffin distils over from the last portion of the tar. It may be obtained in larger quantity by the distillation of "peat" or "Boghead cannel."

II. Action of Acids on Organic Matters.

(1.) *Sulphuric acid.*—This acts on organic bodies in different ways, as follows :—

(α.) It may combine with the organic body. *Examples*:—Organic bases become sulphates. Alcohol (C_2H_6O) becomes sulphovinic acid or acid-ethylic-sulphate (C_2H_5,HSO_4). Benzoic acid ($C_7H_6O_2$) becomes sulpho-benzoic acid ($C_7H_6O_2,SO_3$). Benzol (C_6H_6) becomes sulphobenzolic acid ($C_6H_6.SO_3$). Glycerine ($C_3H_8O_3$) becomes sulphoglyceric acid ($C_3H_8O_3,SO_3$).

(β.) It may decompose the organic body. *Examples*:—Oxalic acid ($C_2H_2O_4 = CO_2 + CO + H_2O$); formic acid ($CH_2O_2 = CO + H_2O$), etc.

(γ.) It may abstract the elements of water from the organic body. *Examples:*—Thus sugar is carbonized by it. Alcohol (C_2H_6O) becomes ether ($C_4H_{10}O$).

(δ.) It may introduce the elements of water into the organic body. *Examples:*—Dextrine ($C_6H_{10}O_5$) becomes glucose ($C_6H_{12}O_6$).

(ε.) It may dissolve the organic body and effect an alteration in its

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color. *Example*:—Salicine is turned a bright red by the action of the acid.

(2.) *Nitric acid.* With some organic bodies (as morphia) nitric acid strikes a deep red colour. The strong acid effects in many cases complete destruction of the substance on which it acts. For example, sugar is broken up into water and carbonic acid. The chemical effects of the dilute acid on organic bodies vary as follows:—

(α.) It may combine with the organic body. *Examples*:—With basic bodies it forms salts. Ethylamine (C_2H_7N) becomes ethylamine nitrate (C_2H_7N,HNO_3)

(β.) It may effect the oxidation of the organic body. *Examples*:—Sugar ($C_{12}H_{22}O_{11}$) and starch ($C_6H_{10}O_5$) form oxalic acid ($C_2H_2O_4$); gum ($C_{12}H_{22}O_{11}$) forms mucic acid ($C_6H_{10}O_8$).

(γ.) It may form substitution products with the organic body. Thus, nitryl (NO_2) may be substituted for hydrogen, forming nitro-compounds, which are generally explosive. *Examples*:—Benzene (C_6H_6) becomes nitro-benzene ($C_6H_5(NO_2)$); cellulin ($C_6H_{10}O_5$) becomes guncotton ($C_6H_7(NO_2)_3O_5$); glycerine ($C_3H_8O_3$) becomes nitro-glycerine ($C_3H_5(NO_2)_3O_3$).

(3.) *The Haloid acids* (HCl; HBr; HI).

(α.) They may *combine with the organic body*, as in the case of the alkaloids, the compound ammonias, and various unsaturated compounds. Examples:—*Ethylamine* (C_2H_7N) becomes ethylammonic chloride (C_2H_7N,HCl); *turpentine* ($C_{10}H_{16}$) becomes hydrochlorate of dadyle, or artificial camphor ($C_{10}H_{16}.HCl$). (The same change occurs by the action of HCl on most essential oils.) *Fumaric acid* ($C_4H_4O_4$) becomes bromo-succinic acid ($C_4H_4O_4,HBr$); *ethylene* (C_2H_4) becomes mono-iodo-ethane (C_2H_4,HI); *hydrocyanic acid* (HCN) becomes hydriodate of formylamine (HCN,HI).

(β.) The substitution of the chlorine, bromine, or iodine of the acid for the group $(HO)'$ may result. This happens more particularly in the case of the alcohols and oxy-acids. *Examples*:—Alcohol ($C_2H_5(HO)$) becomes ethylic iodide (C_2H_5I); oxy-proprionic acid ($C_3H_5(HO)O_2$) becomes bromo-proprionic acid ($C_3H_5BrO_2$).

[In the case of hydriodic acid, it effects the immediate decomposition of the iodine substitution compounds, the iodine being replaced by hydrogen. Thus hydriodic acid is a powerful reducing agent, for it first of all replaces HO by I, and then instantly replaces the I by H.]

(4.) *Phosphoric acid.*—The anhydride acts as a dehydrating agent. *Example*:—Glycerine ($C_3H_8O_3$) becomes acrolein (C_3H_4O).

III. Action of the Fixed Alkaline Hydrates on Organic Bodies.

(1.) They may combine with the organic body, as, *e.g.*, where salts are formed with organic acids, etc. *Examples*:—Potassic acetate. Camphor ($C_{10}H_{16}O$)+KHO forms potassic campholate ($C_{10}H_{17}KO_2$).

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(2.) They may act as oxidising agents, forming acids, with the disengagement of hydrogen. *Example:*—Acetic acid is formed by the action of potassic hydrate on alcohol:—

$$C_2H_6O + KHO = KC_2H_3O_2 + 2H_2.$$
Alcohol + Potassic hydrate = Potassic acetate + Hydrogen.

If the body be a nitrogenised body, the nascent hydrogen combines with the nitrogen to form ammonia.

(3.) On chlorine, or other haloid substitution products, alkalies at times effect (α) the replacement of the halogen by the group (HO), or (β) remove the halogen in part or wholly from the compound.

(α.) $C_2H_5Cl + KHO = KCl + C_2H_5(HO).$
Ethylic chloride + Potassic hydrate = Potassic chloride + Alcohol.

(β.) $C_2H_3Br + KHO = KBr + H_2O + C_2H_2.$
Bromethylene + Potassic hydrate = Potassic bromide + Water + Acetylene.

(4.) The amides (that is, compounds of amidogen $(NH_2)'$ and an acid radical), are decomposed by the alkaline hydrates, their nitrogen being evolved as ammonia, the metal (K or Na) forming a salt with the corresponding acid. *Example:*—Acetamide (NH_2,C_2H_3O) becomes ammonia (NH_3) and potassic acetate (KO,C_2H_3O).

IV. Action of Alkaline Carbonates on Organic Matter.

When an organic body containing nitrogen is fused with an alkaline carbonate, carbonic oxide is evolved, and cyanogen, as a cyanide of the metal, is formed. Thus—

$$K_2CO_3 + C_4 + N_2 = 2KCN + 3CO.$$
Potassic carbonate + Carbon + Nitrogen = Potassic cyanide + Carbonic oxide.

V. Action of the Haloid Elements on Organic Bodies.

(1.) *Chlorine.*

(α.) It may combine with the organic body (forming additive compounds). This happens in the case of certain non-saturated compounds. *Examples:*—Benzene (C_6H_6) becomes benzene hexachloride ($C_6H_6Cl_6$).

(β.) It may in the presence of water, oxidize the organic body. *Example:*—Benzoic aldehyde (C_7H_6O) becomes benzoic acid ($C_7H_6O_2$).

(γ.) It may effect the removal of hydrogen (as HCl) from the organic body with the substitution of chlorine (forming substitution products). This may be complete or partial, depending upon the substance acted upon, the temperature, etc. Thus we have:—

$C_2H_4O_2$ ..... Acetic acid	CH_4 ..... Methane
$C_2H_3ClO_2$ ... Chloracetic acid	CH_3Cl ... Chloromethane
$C_2HCl_3O_2$ ... Trichloracetic acid	CH_2Cl_2... Dichloromethane
	$CHCl_3$ ... Trichloromethane
	CCl_4 ..... Tetrachloromethane

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(δ.) It may effect the removal of hydrogen (as HCl) from the organic body, but without the substitution of chlorine for it. *Example :*—By acting with chlorine on alcohol (C_2H_6O), we form aldehyde (C_2H_4O) ($C_2H_6O + Cl_2 = C_2H_4O + 2HCl$).

(2.) *Bromine.*—The action of bromine is in all respects similar to, but less intense than, that of chlorine.

(3.) *Iodine.*—Like chlorine and bromine, but less intensely than either, iodine forms (1) additive compounds (such as $C_2H_4I_2$) with non-saturated bodies, and (2) also acts as an oxidizing agent. But unlike chlorine and bromine it does not form substitution products by direct combination, unless (1) the hydriodic acid formed, be immediately decomposed by some such means as by the addition of mercuric oxide to the mixture, whereby HgI_2 is formed ($HgO + 2HI = HgI_2 + H_2O$), or iodic acid when free iodine is produced ($HIO_3 + 5HI = 3I_2 + 3H_2O$); or (2) by the double decomposition of other chlorine and bromine compounds with potassic iodide. *For example :*—Iodacetic acid ($C_2H_3IO_2$) may be formed from bromacetic acid ($C_2H_3BrO_2$), by the action upon it of potassic iodide. The intense action of hydriodic acid on iodo-derivatives, explains the difficulty of forming substitution compounds by the direct action of iodine.

VI. Action of Nascent Oxygen on Organic Bodies.

The nascent oxygen for this purpose is commonly liberated by the action of dilute sulphuric acid on potassic dichromate.

1. The oxygen may combine with the organic body. *Example :*—Aldehyde (C_2H_4O) becomes acetic acid ($C_2H_4O_2$).

2. It may decompose the organic body, forming two or more oxidized compounds.

3. It may simply remove hydrogen from the organic body. *Example :*—Alcohol (C_2H_6O) becomes aldehyde (C_2H_4O).

4. It may remove hydrogen from the body, the oxygen replacing it in equivalent quantity. *Example :*—Alcohol (C_2H_6O) becomes acetic acid ($C_2H_4O_2$).

5. It may remove hydrogen, the oxygen replacing it by twice its equivalent quantity. *Example :*—Naphthalene ($C_{10}H_8$) becomes naphtho-quinone ($C_{10}H_6O_2$).

6. If the oxidation be intense, then (as in combustion) the carbon and hydrogen of the organic body may be broken up into water and carbonic anhydride, the sulphur oxidized, and the nitrogen and haloid elements set free.

The changes thus effected by the oxidation of organic bodies, are remarkable, and of great interest. By the action of nascent oxygen on salicine (viz., by distilling it with dilute sulphuric acid and potassic bichromate) we obtain the artificial oil of the spiræa, or meadow-sweet. Uric acid ($C_5H_4N_4O_3$) by oxidation

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becomes alloxan ($C_4H_2N_2O_4$), and alloxan by oxidation becomes urea (CH_4N_2O). By the action of nascent oxygen on amylic alcohol (fusel oil) ($C_5H_{12}O$), we form valerianic acid ($C_5H_{10}O_2$), etc.

VII. Action of Nascent Hydrogen on Organic Bodies.

Free hydrogen has no action on organic bodies; nascent hydrogen acts powerfully. Nascent hydrogen may be set free either by (1) the action of water on sodium amalgam, or (2) by the action of dilute sulphuric acid on zinc, or of hydrochloric acid on tin.

1. The hydrogen may combine with the organic body. *Example:*—Ethene oxide (C_2H_4O) forms alcohol (C_2H_6O).

2. The hydrogen (2 atoms) may remove oxygen (1 atom) from the organic body. *Example:*—Benzoic acid ($C_7H_6O_2$)+H_2 becomes benzoic aldehyde (C_7H_6O)+H_2O.

3. The hydrogen may effect the removal of the haloid elements.

4. The hydrogen may remove oxygen and the haloid elements, and be substituted for them in the compound (inverse substitution). This may happen either (α) in equivalent quantities, or (β) the hydrogen substituted may be only one-half the equivalent of oxygen removed. Thus—

(α.)	C_7H_5O,HO Benzoic acid	+	$2H_2$	=	H_2O	+	C_7H_7,HO. Benzylic alcohol.
(β.)	$C_6H_5(NO_2)$ Nitrobenzene	+	$3H_2$	=	$2H_2O$	+	$C_6H_5(NH_2)$. Aniline.

VIII. Action of Other Reagents on Organic Bodies.

1. Zincic chloride, hydric-potassic sulphate, sulphuric and phosphoric oxides, are dehydrating agents.

2. Phosphoric chloride (PCl_5) either (α) removes hydrogen from the organic body, an equivalent of chlorine being substituted in its place; or (β), removes oxygen from a compound, replacing it by its equivalent of chlorine; or (γ), removes hydroxyl, 1 of HO being replaced by 1 of chlorine.

3. Sulphurous acid is a powerful reducing agent. In the presence of a third body, having a tendency to combine with hydrogen, it decomposes water, and forms sulphuric acid by combining with the oxygen, hydrogen being set free.

4. Chromic acid. This acts as a powerful oxidising agent on organic bodies.

We may notice lastly—

IX. The Action of Light and Electricity on Organic Bodies.

(1.) *The action of light.*—The combination of chlorine with many organic bodies, is as much influenced by light as the combination of

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chlorine and hydrogen. Thus chlorine and benzene combine immediately in bright sunlight, slowly in diffused light, but not at all in the dark. The decomposition of hydrocyanic acid is greatly accelerated by light: hence the acid is preserved in blue bottles. Moreover, in some cases the compound formed differs according to the intensity of the light; thus a mixture of chlorine and mono-chloro-propylene (C_3H_5Cl) forms di-chloro-propylene ($C_3H_4Cl_2$) in the dark, but the compound ($C_3H_5Cl_3$) in bright sunlight.

A well known action of light is its power of forming the green chlorophyll of leaves; but we note also a special action of sunlight in elaborating organic compounds generally, in the organisms of growing plants.

(2.) *The action of the galvanic current.* The organic body is often decomposed, oxygen being formed at the positive pole, and hydrogen at the negative (from the decomposition of the water), these bodies acting powerfully in their nascent condition on the organic compound.

Professor J. H. Gladstone and Mr. Tribe have published a series of researches on the action of what they call the copper-zinc couple; that is, a very intimate mixture of powdered copper and zinc. By means of the galvanic power generated by the action of this mixed metallic powder, the preparation and the decomposition of many organic compounds have been effected. *For example*—the preparation of zinc ethyl ($Zn(C_2H_5)_2$), ethyl hydride ($C_2H_5.H$), diamyl, zinc amyl ($Zn(C_5H_{11})_2$), amyl hydride ($C_5H_{11}.H$), methyl hydride ($CH_3.H$), acetylene (C_2H_2), propylene (C_3H_6), propyl hydride ($C_3H_7.H$); also the discovery of zinc propyl ($Zn(C_3H_7)_2$), zinc isopropyl, zinc propiodide ($ZnC_3H_7.I$), and the ethylo-haloid compounds (as ZnC_2H_5Br); also the isolation of diallyl, the conversion of nitrates into ammonia (Thorpe), etc., etc. (*See* "Chemical News" for years 1873–1876.)

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CHAPTER XXI.

CYANOGEN AND ITS COMPOUNDS.

Cyanogen—Hydrocyanic Acid—Cyanides—Compounds of Cyanogen with the Haloids and with Hydroxyl—Sulphocyanic Acid—Double Cyanogen Salts—The Nitroprussides—Prussian Blue—Reactions of Cyanogen Compounds.

CYANOGEN.

CN *or* Cy. *Molecular weight*, 52. *Molecular volume*, [ ]. *Specific gravity*, 1·801. *Fuses at* —29·2° F. (—34° C.). *Boils at* —5·3° (—20·7° C.).

Derivation.—(κύανος blue; γεννάω I produce.)

History.—Discovered by Gay Lussac (1815).

Natural History.—It is not found in nature in a free state. It is met with in the gases issuing from blast furnaces, and is produced in small quantities during the distillation of pit coal.

Preparation.—(1.) By the action of heat on the cyanides of mercury, silver, or gold ($Hg(CN)_2 = Hg + (CN)_2$). [A brown amorphous, insoluble, non-volatile substance (paracyanogen $(CN)_n$) is formed simultaneously with cyanogen. At a heat of 1548° F. (860° C.) paracyanogen is converted solely into gaseous cyanogen, without leaving any residue, thus proving it to be an isomer of cyanogen.]

(2.) By the dry distillation of ammonic oxalate $[(NH_4)_2 C_2O_4]$ or of oxamide $[C_2O_2(NH_2)_2]$.

$(NH_4)_2C_2O_4$	=	$4H_2O$	+	$(CN)_2$.
Ammonic oxalate	=	Water	+	Cyanogen.

Properties.—(α.) *Physical.* A colorless gas, having the odour of bitter almonds. It is intensely poisonous. Its specific gravity is 1·801, and its relative weight 26; 100 cubic inches weigh 55·714 grs., and 1 litre, 2·3296 grms. A pressure of four atmospheres at 45° F. (7·2° C.) or a cold of —22° F. (—30° C.) condenses it to a colorless liquid, which has a specific gravity of 0·87°, and freezes at—29·2° F.(—34° C.). It withstands a very high temperature without decomposing. It is soluble in water (4 vols. in 1 of water), and very soluble in alcohol.

(β.) *Chemical.* Cyanogen burns in air with a rose-red flame, generating CO_2 and N. Exploded with oxygen (1 vol. of Cy and 2 vols. of O) it yields N (1 vol.) and CO_2 (2 vols.). Its solutions (whether aqueous or alcoholic) decompose rapidly, the *primary* products being ammonic oxalate $[(NH_4)_2 C_2O_4]$, a brown insoluble matter (azulmic acid), and traces of hydrocyanic (HCN) and cyanic acids (CNOH). As *secondary* products, formed by the action of the cyanic acid on the water, we obtain urea $CO(NH_2)_2$ and hydric ammonic carbonate NH_4HCO_3.

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The decomposition of the aqueous solution is much retarded by the presence of a mineral acid. Cyanogen was the first well-recognised "compound organic radical." Chemically it behaves exactly like a monad non-metallic element, or simple acid chlorous radical, such as chlorine. Just as chlorine $(Cl)'$ is univalent, the molecule being represented by Cl_2, so cyanogen $(CN)'$ is univalent, its molecule being represented by $(CN)_2$. As chlorine combines with metals to form chlorides (as $AgCl$; $Hg''Cl_2$), so cyanogen combines with metals to form cyanides ($Ag(CN)$; $Hg''(CN)_2$). As chlorine replaces monad elements, so cyanogen replaces monad elements. Cyanogen combines with hydrogen to form hydrocyanic acid (HCN), as chlorine forms hydrochloric acid (HCl).

The reactions of cyanogen with potassic hydrate again, are exactly analogous to those of chlorine. Thus:—

(α.)	$2KHO$	+	Cl_2	=	KCl	+	$KClO$	+	H_2O.
	Potassic hydrate	+	Chlorine	=	Potassic chloride	+	Potassic hypochlorite	+	Water.
(β.)	$2KHO$	+	$(CN)_2$	=	$K(CN)$	+	$K(CN)O$	+	H_2O.
	Potassic hydrate	+	Cyanogen	=	Potassic cyanide	+	Potassic cyanate	+	Water.

Thus cyanogen supplies us with a typical illustration of "a compound radical,"—that is, a group of elements, capable of acting exactly as though it were an element. To express this quasi-elementary character of cyanogen, we represent it by the symbol Cy.

Hydrocyanic Acid (Prussic Acid) (HCN or HCy).

Molecular weight, 27. *Molecular Volume*, [ ]. *Specific gravity of liquid at* 44·9° F. (7·2° C.) 0·7058. *Fuses at* 5° F. (15° C.) *Boils at* 79·7° F. (26·5° C.).

History.—Discovered by Scheele (1782), who named it *prussic acid.* Its composition was proved by Berthollet (1787).

Natural History.—It is found in cherry-laurel water (aqua laurocerasi), in bitter-almond water, and in water distilled in contact with various plants belonging to the N.O. Rosaceæ, and with the kernels of many stone fruits. Its formation in these is no doubt due to the ferment action of emulsin or synaptase on the amygdalin or some body of a similar nature (*see* page 486). It exists, however, ready formed in the juice of the bitter cassava.

Preparation.—(1.) By passing electric sparks through a mixture of nitrogen and acetylene.

N_2	+	C_2H_2	=	$2HCN$.
Nitrogen	+	Acetylene	=	Hydrocyanic acid.

(2.) *Process of B.P. in preparing acidum hydrocyanicum dilutum.*
By distilling potassic ferrocyanide with dilute sulphuric acid—

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$2K_4FeCy_6 + 3H_2SO_4 = 6HCN + K_2Fe_2Cy_6 + 3K_2SO_4$.

Potassic ferrocyanide + Sulphuric acid = Hydrocyanic acid + Ferrocyanide of iron and potassium + Potassic sulphate.

The B.P. solution is made to have a specific gravity of 0·997, and to contain 2 per cent of anhydrous acid; in other words, 100 grains of the dilute acid should yield 10 grains of AgCy when heated with argentic nitrate.

(3.) By the action of acids on metallic cyanides ($KCN + HCl = HCN + KCl$).

Preparation of Scheele's Acid.—Prussian blue and mercuric oxide (HgO) are boiled in water, whereby Fe_2O_3 is precipitated, and a solution of mercuric cyanide ($HgCy_2$) formed. The clear filtrate is then mixed with dilute sulphuric acid, and shaken up with iron filings ($HgCy_2 + Fe + H_2SO_4 = 2HCy + FeSO_4 + Hg$). The solution contains 4 or 5 per cent. of anhydrous acid.

(4.) By heating together chloroform and ammonia. The process is facilitated by the addition of an alcoholic solution of potassic hydrate.

$CH.Cl_3 + NH_3 = HCN + 3HCl$.

Chloroform + Ammonia = Hydrocyanic acid + Hydrochloric acid.

(5.) *Preparation of anhydrous acid.*—By decomposing argentic cyanide (gently heated) with sulphuretted hydrogen, or with gaseous hydrochloric acid.

$2AgCN + H_2S = Ag_2S + 2HCN$.

Argentic cyanide + Sulphuretted hydrogen = Argentic sulphide + Hydrocyanic acid.

Properties.—(α.) *Physical.* A colorless, highly volatile liquid, having a bitter almond odor and a bitter taste. It freezes at 0° F. (—19·8°C.), and boils at 79°F. (26·1° C.), emitting a combustible vapor. The anhydrous acid is so volatile that during its spontaneous evaporation it freezes the rest of the acid. It mixes with water and alcohol in all proportions. Its physiological action is intense, destroying life rapidly. It is given in medicine internally, and, when very much diluted with air, is occasionally used as an inhalation (vapor acidi hydrocyanici (B.P.)).

(β.) *Chemical.* Its acid properties are so feeble that it cannot even displace carbonic acid from its compounds. Both the pure acid and the aqueous solution decompose spontaneously (particularly when exposed to the light), a brown substance called paracyanogen $(CN)_n$ being deposited, and ammonic oxalate and formate produced. A trace of mineral acid, such as is certain to be present in the B.P. acid, retards the decomposition. [It is worthy of note that when ammonic formate is heated, it yields hydrocyanic acid and water ($CNH_4HO_2 = CNH + 2H_2O$)]. It forms with the haloid acids crystalline bodies, such as (HCN.HCl), etc., which are easily decomposed into formic acid and ammonic salts ($HCN.HCl + 2H_2O = CH_2O_2$ (formic acid) +

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NH_4Cl). It forms metallic cyanides with metallic oxides and hydrates, but when boiled with an excess of potash it evolves ammonia.

The Cyanides, Chlorides, and Hydroxides of Cyanogen.

The following constitute the most important of these compounds :—

I. Cyanides.

	Formula.	Molecular Weight.	Specific Gravity.	Appearance.	
Potassic cyanide	KCy	65		White cubes	Deliquescent; soluble in water and spirit; fusible. They are not changed by heat when air is excluded, but in the presence of air they become cyanates. Their solutions, when boiled, yield formates. Solutions alkaline.
Sodic cyanide	NaCy	49		do.	
Ammonic cyanide ..	NH_4Cy	44		do.	Very soluble; the solution easily decomposes.
Mercuric cyanide.. ..	$HgCy_2$	252		do.	Soluble in water and alcohol; solution not precipitated by alkalies.
Argentic cyanide	AgCy	134		do.	Insoluble.
Zincic cyanide	$ZnCy_2$	91		do.	Do.
Cobaltous cyanide ..	$CoCy_2$	111		do.	Do.
Palladious cyanide ..	$PdCy_2$	158		Yellowish white	Do.
Auric cyanide	$AuCy_3$	275		do.	Insoluble, soluble in KCy.
Ferrous cyanide	$FeCy_2$	108		Yellowish red	Soluble in KCy, forming $(K_4Cy_4Fe''Cy_2)$.
Ferric cyanide	Fe_2Cy_6				Only known in solution.

II. Haloid Salts.

Cyanic chloride (gaseous) .. .. CyCl.
,, (liquid) .. .. Cy_2Cl_2.
,, (solid) .. .. Cy_3Cl_3.
Cyanic bromide .. .. CyBr.
,, ... Cy_3Br_3.
Cyanic iodide .. .. CyI.
Cyanic sulphide .. .. Cy_2S.

III. Hydroxides, Etc.

Cyanic acid.. .. CyOH
- Potassic cyanate .. .. KCyO.
- Ammonic cyanate .. .. NH_4CyO.
- Urea .. .. CH_4N_2O.

Cyanuric acid .. $Cy_3O_3H_3$
- Argentic cyanurate .. $Ag_3Cy_3O_3$.
- Argentic hydric cyanurate $Ag_2HCy_3O_3$.
- Potassic hydric cyanurate.. $KH_2Cy_3O_3$.

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Fulminuric acid	.. $Cy_3O_3H_3$..	Potassic hydric fulminurate	$K_2HCy_3O_3$.
Cyamelide ..	.. $Cy_nO_nH_n$		
Fulminic acid	.. $Cy_2H_2O_2$ (?)	Mercuric fulminate	$Hg''Cy_2O_2$.
		Argentic fulminate	$Ag_2Cy_2O_2$.
		Ammonic argentic fulminate	$NH_4AgCy_2O_2$.
Sulphocyanogen ..	CNS or CyS or Scy	Ammonic sulphocyanate..	NH_4CyS.
Sulphocyanic acid ..	HCyS	Potassic sulphocyanate ..	KCyS.
		Plumbic sulphocyanate ..	$Pb(CyS)_2$.
		Mercuric sulphocyanate ..	$HgCy_2S_2$.

The Cyanides.

The cyanides are closely allied to the haloid salts.

Preparation of Metallic Cyanides.

1. By burning the metal in cyanogen gas, or in the vapor of hydrocyanic acid (KCy; NaCy).

Ammonic cyanide may be formed by mixing together the vapors of ammonia and hydrocyanic acid.

2. By acting on metallic oxides or hydrates with hydrocyanic acid:

(α.) $HgO + 2HCy = Hg''Cy_2 + H_2O$

(β.) $KHO + HCy = KCy + H_2O$.

3. By passing nitrogen over a red-hot mixture of a metallic carbonate and carbon :—

K_2CO_3	+	4C	+	2N	=	2KCN	+	3CO.
Potassic carbonate	+	Carbon	+	Nitrogen	=	Potassic cyanide	+	Carbonic oxide.

Thus cyanogen is formed in blast furnaces, the potassic carbonate being supplied by the ash, and the C and N by the fuel. Ammonic cyanide may be formed by passing ammonia gas over red-hot charcoal.

4. In the case of potassic cyanide it may be prepared either—

(α.) By merely heating potassic ferrocyanide,—

$K_4Fe''Cy_6$	=	4KCy	+	FeC_2	+	N_2.
Potassic ferrocyanide	=	Potassic cyanide	+	Carbide of iron	+	Nitrogen.

(β.) Or, by heating a mixture of potassic ferrocyanide and potassic carbonate.

$K_4Fe''Cy_6$	+	K_2CO_3	=	5KCy	+	KCyO	+	Fe	+	CO_2.
Potassic ferrocyanide	+	Potassic carbonate	=	Potassic cyanide	+	Potassic cyanate	+	Iron	+	Carbonic anhydride.

[Prepared in this way commercial potassic cyanide usually contains both potassic cyanate and potassic carbonate.]

If mercuric sulphate be added to the potassic ferrocyanide, mercuric cyanide is formed.

5. By the action of a soluble cyanide, or of hydrocyanic acid, on metallic salts.

(α.) Thus *potassic cyanide*, with ammonic chloride, forms ammonic

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cyanide; with mercuric oxide, mercuric cyanide; with palladious chloride, palladious cyanide, etc.

(β.) Thus *hydro-cyanic acid* with zinc acetate, forms zincic cyanide, etc.

Properties of the Cyanides.—They are all more or less of a white color, and have a bitter-almond odor. In the case of potassic cyanide, it evolves an odor of almonds (from the free hydro-cyanic acid present) and ammonia (from the decomposition of the cyanate by moisture).

$$2KCyO + 4H_2O = K_2CO_3 + (NH_4)_2CO_3.$$

Potassic cyanate + Water = Potassic carbonate + Ammonic carbonate.

All the cyanides are poisonous bodies.

The alkaline cyanides, when fused in the presence of air, become cyanates. Acids decompose certain cyanides readily, such as potassic cyanide (which is even decomposed by carbonic acid), whilst on other cyanides, as aurous cyanide, they act with difficulty. Most cyanides are soluble in solutions of the alkaline cyanides, forming double cyanides. So rapid is this combination in some cases (as with ferrous and ferric cyanides), that the simple cyanides can scarcely be said to exist in a separate state.

Uses.—Potassic cyanide is the most important of the cyanides. It is used (α) in *electro-plating and gilding*, from its property of dissolving argentic cyanide, forming with it a compound which is easily decomposed with the battery; (β) *in photography*, from its property of dissolving silver, either as a chloride, bromide, iodide, or as the metal; and (γ) *in the laboratory*, as a reducing agent, from its property of abstracting oxygen from bodies at a high temperature to form a cyanate ($SnO_2 + 2KCy = Sn + 2KCyO$).

Cyanogen Chlorides, etc.

Three isomeric chlorides of cyanogen have been described. They are all the products of the action of chlorine on hydrocyanic acid, or on a metallic cyanide:—

Gaseous Cyanic Chloride ($CyCl = 61{\cdot}5$. Mol. Vol.) is a colorless pungent gas, capable of being liquefied by a pressure of four atmospheres. It is soluble in water, alcohol and ether. On being passed into a solution of ammonia in anhydrous ether, it forms cyanamide CN_2H_2.

Liquid Cyanic Chloride ($Cy_2Cl_2 = 123$. Mol. Vol.) is an oily liquid, boiling at 59·9° F. (15·5° C.), and freezing at 23° F. (−5° C.). Preserved in hermetically-sealed tubes for some time, it assumes the solid modification.

Solid Cyanic Chloride ($Cy_3Cl_3 = 184{\cdot}5$. Mol. Vol.) is a crystalline colorless solid. It is soluble in alcohol and ether. It

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melts at 284° F. (140° C.), and at a higher temperature sublimes unchanged.

This body yields, by distillation, *cyanic acid* (HCyO), and by the action of water, its polymer *cyanuric acid* ($H_3Cy_3O_3$).

The **Cyanic Bromides** (CyBr and Cy_3Br_3), and a solid crystalline **Cyanic Iodide** (CyI), have been prepared. By the action of the latter on sulpho-cyanate of silver, a **Cyanic Sulphide** (Cy_2S) is formed.

COMPOUNDS OF CYANOGEN AND HYDROXYL.

Cyanic acid	CyOH.
Cyanuric acid	$Cy_3O_3H_3$.
Fulminuric acid	$Cy_3O_3H_3$.
Cyamelide	$Cy_nO_nH_n$.

Cyanic Acid (CyOH or CN(OH)=43) and the **Cyanates.**

(*α.*) *Preparation of the acid.*—By the distillation of dry cyanuric acid ($Cy_3O_3H_3$) into an ice-cold receiver.

(*β.*) *Preparation of the cyanates* (M'CNO).—(1.) By the direct oxidation of the cyanides ($KCy + PbO = Pb + KCNO$).

(2.) By the action of cyanogen gas upon potassic hydrate ($(CN)_2 + 2KHO = KCN + KCNO + H_2O$). The acid cannot be prepared by the addition of acids to the salts, inasmuch as it forms, by combination (*α*) with *water*, ammonic carbonate, and (*β*) with *ammonia*, urea, or ammonic cyanate. Thus—

(*α.*) $Cy(OH) + 2H_2O = NH_4HCO_3$ (ammonic carbonate);

(*β.*) $Cy(OH) + NH_3 = CH_4N_2O$ (urea).

Properties.—Cyanic acid is a colorless, pungent, acid liquid. It changes rapidly at 32° F. (0° C.) into cyamelide. It is monobasic.

Ammonic Cyanate (NH_4CyO); *urea* (CH_4N_2O).

Preparation.—(1.) When cyanic acid vapor is mixed with an excess of ammonia, ammonic cyanate is formed. After a short time by exposure to air, or immediately at 212° F. (100° C.), the salt undergoes a molecular change, and becomes urea. (Wöhler.)

(2.) *Ammonic cyanate* and *urea* may also be prepared by mixing potassic cyanate and ammonic sulphate in water, evaporating to dryness, and dissolving out the urea from the residue with alcohol.

$2KCyO$	+	$(NH_4)_2SO_4$	=	K_2SO_4	+	$2NH_4CyO$.
Potassic cyanate	+	Ammonic sulphate	=	Potassic sulphate	+	Ammonic cyanate.

Urea is a weak base, and constitutes the chief nitrogenised compound of urine. It may be obtained as a nitrate [$(CN_2H_4O)HNO_3$] by adding nitric acid to concentrated urine. The aqueous solution, when mixed with oxalic acid, forms an insoluble oxalate of urea—

$$[(CN_2H_4O)C_2H_2O_4].$$

It is decomposed by heat, giving off ammonia, the residue constituting cyanuric acid.

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In contact with decomposing matter, urea combines with water and becomes ammonic carbonate. Hence the presence of the latter in decomposed urine.

$$\underset{\text{Urea}}{CN_2H_4O} + \underset{\text{Water}}{2H_2O} = \underset{\text{Ammonic carbonate.}}{(NH_4)_2CO_3}.$$

A compound where the oxygen of the urea has been replaced by sulphur, forming what is called *sulphur-urea* (CN_2H_4S), has been obtained.

Cyanuric Acid ($Cy_3O_3H_3$ or $C_3N_3(OH)_3$).

Preparation.—(1.) By the action of heat on urea.

(2.) By the action of water on solid cyanic chloride ($Cy_3Cl_3 + 3H_2O = 3HCl + Cy_3H_3O_3$). [As water replaces the Cl of cyanic chloride by the group HO, so phosphorus pentachloride replaces the group HO of cyanuric acid by Cl, ($C_3N_3(OH)_3 + 3PCl_5 = C_3N_3Cl_3 + 3POCl_3 + 3HCl$)].

Properties.—It forms colorless efflorescent crystals, which are not soluble in cold water, but are soluble in boiling (1 in 24). The acid is very stable, and is dissolved, but not decomposed, by strong sulphuric or by nitric acid. In this respect it contrasts remarkably with its isomer cyanic acid.

It is a tribasic acid, and forms three classes of salts: viz., $M'_3Cy_3O_3$ (as $Ag_3Cy_3O_3$), $M'_2HCy_3O_3$ (as $Ag_2HCy_3O_3$), and $M'H_2Cy_3O_3$ (as $KH_2Cy_3O_3$).

Fulminuric Acid ($Cy_3O_3H_3$ or $C_3N_3(OH)_3$).

Preparation.—By the action of a soluble chloride on mercuric fulminate.

$$\underbrace{3Hg''Cy_2O_2}_{\text{Mercuric fulminate.}} + 8KCl + H_2O = 4KCl + 2HgCl_2 + Hg''O + \underbrace{2K_2HCy_3O_3}_{\text{Potassic fulminurate.}}$$

Fulminuric acid, unlike cyanuric acid (both of which have the same composition), is monobasic.

Cyamelide ($Cy_nO_nH_n$, or $Cy_n(HO)_n$.—A white, solid, amorphous body, formed spontaneously from cyanic acid. It is insoluble either in dilute acids, in alcohol, in ether, or in water. By dry distillation it yields cyanic acid.

The relationship of these bodies requires notice:—

1. Cyanic acid may be prepared by heat from cyanuric acid.
2. Ammonic cyanate forms urea.
3. Urea by heat forms cyanuric acid.
4. Cyanic acid changes spontaneously to cyamelide.
5. Cyamelide by dry distillation yields cyanic acid.

Fulminic Acid.—This acid has never been isolated. Its probable composition is $H_2Cy_2O_2$. Thus it is polymeric both with cyanic and with cyanuric acids. It is a bibasic acid.

The fulminates are highly explosive bodies. They are formed by dissolving the metal in nitric acid and adding alcohol.

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Fulminate of Mercury ($Hg''Cy_2O_2$) has a specific gravity of 4·4, and is decomposed either by a temperature of 360° F. (182·2° C.), or by being touched with sulphuric or nitric acid, carbonic oxide, nitrogen, and the free metal being produced. Thus:—

$$Hg''Cy_2O_2 = Hg + 2CO + N_2.$$

Fulminate of Silver has the composition $Ag_2Cy_2O_2$, and is even more easily decomposed than mercuric fulminate.

Double Fulminates have also been prepared, as, *e. g.*, $NH_4AgCy_2O_2$ and $AgKCy_2O_2$.

Sulphocyanic Acid (HCNS, or HCyS). This is the sulphur analogue of cyanic acid.

Preparation.—By decomposing lead sulphocyanate suspended in water, with sulphuretted hydrogen.

Properties.—As prepared above, it is a colorless acid solution, from which the acid may be obtained as a solid crystalline body by cold. It is decomposed by boiling, and also by exposure to air. The acid is monobasic, and forms salts called sulphocyanates.

Ammonic Sulphocyanate (NH_4CyS) is prepared by neutralizing the acid with ammonia, or by digesting hydrocyanic acid with yellow ammonic sulphide. By its distillation at a high temperature a body called Melam ($C_6H_9N_{11}$) is formed. Melam, by the action of potassic hydrate and heat, forms Mellamine ($C_3H_6N_6$).

Potassic Sulphocyanate (KCyS) is prepared either (1) by fusing together potassic cyanide and sulphur, or (2) by fusing together three parts of potassic ferrocyanide, one part of potassic carbonate, and two parts of sulphur, in a covered crucible. The mass is then lixiviated, and the salt crystallised from the solution:—

$$K_4Fe''Cy_6 + S_6 = 4KCyS + Fe''(CyS)_2.$$

By the action of chlorine on a solution of potassic sulphocyanate, a yellow insoluble precipitate is formed of *persulphocyanogen* (Cy_3HS_3), which when heated forms a body called *mellone* (C_9H_{13}), an organic radical, which with hydrogen forms an acid called *hydro-mellonic acid* ($H_3C_9H_{13}$). The salts are called *mellonides*, as the potassic mellonides ($K_3C_9H_{13}$; $K_2HC_9H_{13}$ and $KH_2C_9H_{13}$). The tripotassic mellonide yields insoluble precipitates with salts of silver, mercury, lead, etc., viz., *argentic mellonide* ($Ag_3C_9H_{13}$); *mercuric mellonide* ($Hg_3(C_9H_{13})_2$); *plumbic mellonide* ($Pb_3(C_9H_{13})_2$).

Plumbic Sulphocyanate ($Pb(CyS)_2$) is prepared by acting on potassic sulphocyanate with lead acetate.

Mercuric Sulphocyanate ($Hg''(CyS)_2$) constitutes the toy known as Pharaoh's Serpents.

These bodies are represented as containing the compound radical *sulphocyanogen* (CyS or Scy).

The *selenio-cyanates* correspond to the sulphocyanates, and have the formula (M'CNSe).

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Double Salts, etc., of Cyanogen.

	Formula.
Ferrocyanogen	$Fe''Cy_6$
Ferrocyanic acid	$H_4Fe''Cy_6$
Potassic ferrocyanide	$K_4Fe''Cy_6$
Cupric ferrocyanide	$Cu''_2Fe''Cy_6$
Plumbic ferrocyanide	$Pb_2Fe''Cy_6$
Ferric ferrocyanide (Prussian blue)	$Fe'''_4Fe''_3Cy_{18}$
Potassic ferrous ferrocyanide (Everitt's white salt)	$FeK_2Fe''Cy_6$
Potassic nickelous cyanide	$K_2Ni''Cy_4=2KCy,NiCy_2$
Ferricyanogen	$Fe'''Cy_6$
Ferricyanic acid	$H_3Fe'''Cy_6$
Potassic ferricyanide	$K_3Fe'''Cy_6$
Plumbic ferricyanide	$Pb''_3Fe'''_2Cy_{12}$
Ferrous ferricyanide (Turnbull's blue)	$Fe''_3Fe'''_2Cy_{12}$
Potassic ferrous ferricyanide	$Fe''KFe'''Cy_6$
Hydro-nitro-prussic acid	$H_2(NO)Fe''Cy_5$
Sodic nitro-prusside	$Na_2(NO)Fe''Cy_5$

Double Cyanides.

These consist of compounds of an alkaline cyanide or a cyanide of an alkaline earth, with a cyanide of another metal.

Preparation.—By dissolving a cyanide of a heavy metal in an alkaline cyanide.

Properties.—The double cyanides may be divided into two classes:—

(α.) The *unstable double cyanides*, which are very poisonous, and are decomposed by a dilute acid (as HCl), hydrocyanic acid being liberated from the alkaline cyanide, either with the precipitation of the metallic cyanide, or with the conversion of both metals into chlorides. Thus :—

$$K_2Ni''Cy_4 + 2HCl = NiCy_2 + 2KCl + 2HCy.$$

Potassic nickelous cyanide + Hydrochloric acid = Nickelous cyanide + Potassic chloride + Hydrocyanic acid.

(β.) The *stable double cyanides*, which are not poisonous. They are not decomposed, like the above, by a dilute acid, but one of the metals unites with hydrogen to form an acid. Thus :—

$$K_4Fe''Cy_6 + 4HCl = H_4FeCy_6 + 4KCl.$$

Ferrocyanide of potassium + Hydrochloric acid = Hydroferrocyanic acid + Potassic chloride.

The ferrocyanides and ferricyanides are of importance. The pure cyanides of iron, owing to their strong tendency to form double salts have never been prepared.

Ferrocyanogen and **Ferricyanogen.**—These groups, neither of which have been isolated, constitute two compound radicals containing iron, differing from one another only in this, that in ferrocyanogen the iron is *bivalent*, whilst in ferricyanogen it is *trivalent*. Thus:—

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Ferrocyanogen.—$Fe''Cy_6$ forms potassic ferrocyanide ($K_4Fe''Cy_6$).
Ferricyanogen.—$Fe'''Cy_6$,, potassic ferricyanide ($K_3Fe'''Cy_6$, or $K_6(Fe_2)^{vi}Cy_{12}$).

It will be further noticed that a ferrocyanide differs only from a ferricyanide by one atom of a monad metal (such as K′); hence (*α*) *oxidizing agents* (as Cl and HNO_3) convert ferrocyanides into ferricyanides, whilst (*β*) *reducing agents* (*i. e.*, agents capable of undergoing oxidation or of giving up hydrogen) convert ferricyanides into ferrocyanides. To express the radical ferrocyanogen briefly, the formula (Fcy) is frequently used.

Analogous to ferricyanogen we have compound radicals, where the iron is displaced by other metals, as *cobalticyanogen* ($CoCy_6$), *platinocyanogen* ($PtCy_4$), etc. These bodies are distinguished by forming acids with hydrogen, from which salts may be prepared by the displacement of hydrogen.

Ferrocyanic Acid ($H_4Fe''Cy_6$).

Preparation.—(1.) By decomposing plumbic (or cupric) ferrocyanide, suspended in water, with sulphuretted hydrogen.

(2.) By decomposing a strong solution of potassic ferrocyanide with hydrochloric acid.

K_4FeCy_6	+	$4HCl$	=	$H_4Fe''Cy_6$	+	$4KCl$.
Potassic ferrocyanide	+	Hydrochloric acid	=	Hydroferrocyanic acid	+	Potassic chloride.

Properties.—A white, crystalline, soluble substance, decomposed by heat into hydrocyanic acid and ferrous cyanide ($H_4FeCy_6 = 4HCy + FeCy_2$), the ferrous cyanide forming Prussian blue by exposure to air ($9FeCy_2 + O_3 = {}'Fe'''_4Fe''_3Cy_{18} + Fe_2O_3$). The acid is tetrabasic, and forms salts called ferrocyanides ($M'_4Fe''Cy_6$).

Potassic Ferrocyanide.—*Yellow prussiate of potash* ($K_4Fe''Cy_6$, or $4KCy,Fe''Cy_2$, or K_4Fcy, or $K_4Fe(CN)_6$).

Preparation.—(1.) By the action on potassic cyanide, either (*α*) of iron filings, the mixture being freely exposed to the air, or (*β*) of ferrous hydrate.

(*α*.)	$6KCy$	+	Fe	+	H_2O	+	O	$= K_4Fe''Cy_6 +$	$2KHO$.
	Potassic cyanide	+	Iron	+	Water	+	Oxygen	= Potassic ferrocyanide +	Potassic hydrate.

(*β*.)	$6KCy$	+	FeH_2O_2	=	$K_4Fe''Cy_6$	+	$2KHO$.
	Potassic cyanide	+	Ferrous hydrate	=	Potassic ferrocyanide	+	Potassic hydrate.

(2.) By digesting potassic cyanide, either (*α*) with ferrous sulphide, or (*β*) with a soluble ferrous salt.

(*α*.)	$Fe''S$	+	$6KCy$	=	$K_4Fe''Cy_6$	+	K_2S.
	Ferrous sulphide	+	Potassic cyanide	=	Potassic ferrocyanide	+	Potassic sulphide.

(*β*.)	$FeSO_4$	+	$6KCy$	=	$K_4Fe''Cy_6$	+	K_2SO_4.
	Ferrous sulphate	+	Potassic cyanide	=	Potassic ferrocyanide	+	Potassic sulphate.

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(3.) The ordinary process of manufacturing "yellow prussiate" is as follows:—Nitrogenised animal matters, such as horns, parings of hides, blood, etc., are fused with crude potassic carbonate and scraps of old iron, in covered iron vessels. Thus—(*a.*) A *potassic cyanide* is formed—

K_2CO_3	+	C_4	+	N_2	=	KCN	+	3CO.
Potassic carbonate	+	Carbon	+	Nitrogen	=	Potassic cyanide	+	Carbonic oxide.

(*β.*) And also a *ferrous sulphide*, from the combination of the iron with the sulphur derived partly from the animal matter, and partly from the K_2SO_4 present in the crude potassic carbonate.

The fused mass is now treated with boiling water, when the ferrous sulphide re-acts (as in process 2 (*a*)) on the potassic cyanide, forming sulphide and ferrocyanide of potassium, the separation of the latter being easily effected by solution and crystallisation ($FeS + 6KCy = K_4FeCy_6 + K_2S$). Sometimes, to avoid the formation of potassic sulphide, pure potassic carbonate is used, and the cyanides formed afterwards digested with ferrous carbonate:—

$FeCO_3$	+	6KCy	=	$K_4Fe''Cy_6$	+	K_2CO_3.
Ferrous carbonate	+	Potassic cyanide	=	Potassic ferrocyanide	+	Potassic carbonate.

Properties.—It forms large, tough, yellow crystals ($K_4FeCy_6 + 3H_2O$), soluble in both cold and hot water (1 in 4 at 60° F.; 1 in 2 at 212° F.), and insoluble in alcohol. It is not poisonous.

At a moderate heat the yellow salt becomes white and anhydrous. Heated intensely *in air*, it forms potassic cyanate; but heated *without air* it forms potassic cyanide, carbide of iron, etc.

With dilute sulphuric acid, it yields hydrocyanic acid, but with strong sulphuric acid, the salt is decomposed ($K_4Fe''Cy_6 + 6H_2SO_4 + 6H_2O = 6CO + FeSO_4 + 2K_2SO_4 + 3[(NH_4)_2SO_4]$). By the action of hydrochloric acid, hydroferrocyanic acid is precipitated (H_4FeCy_6).

Fused with alkaline carbonates, it forms potassic cyanide.

With neutral or acid solutions of many metallic salts, it gives characteristic precipitates. With *ferrous salts*, it forms a light blue potassio-ferrous ferrocyanide ($Fe''K_2Fe''Cy_6$); with *ferric salts*, ferric ferrocyanide or Prussian blue ($'Fe'''_4Fe''_3Cy_{18}$); with *cupric salts*, a red cupric ferrocyanide ($Cu''_2Fe''Cy_6$); with *lead salts*, a plumbic ferrocyanide (Pb_2FeCy_6), etc.

The precipitate with *cobalt*, is yellowish green; with *uranium*, brown; and with *zinc*, *cadmium*, *nickel*, *manganese*, *tin*, *lead*, *bismuth*, *antimony*, *silver*, and *mercury*, white. Except the precipitates with zinc and cadmium, they are all insoluble in dilute hydrochloric acid.

Uses.—It is largely used in the manufacture of Prussian blue (*see* page 521), in the preparation of hydrocyanic acid (*see* page 509), etc.

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Ferricyanic Acid (H_3FeCy_6).

Preparation.—By decomposing plumbic ferricyanide ($Pb_3Fe'''_2Cy_{12}$), suspended in water, with sulphuric acid.

Properties.—A red unstable liquid. By heat, it forms hydrocyanic acid and a hydrated ferric cyanide ($Fe_2Cy_6,3H_2O$).

Potassic Ferricyanide.—*Red prussiate of potash* ($K_3Fe'''Cy_6$, or $3KCy,Fe''Cy_3$, or $K_6(Fe_2)^{vi}Cy_{12}$).

Preparation. By the action of an oxidizing agent (such as nitric acid, chlorine, etc.,) on potassic ferrocyanide :—

$2(K_4Fe''Cy_6)$	+	Cl_2	=	$2(K_3Fe'''Cy_6)$	+	$2KCl$.
Potassic ferrocyanide	+	Chlorine	=	Potassic ferricyanide	+	Potassic chloride.

The chlorine withdraws one-fourth of the potassium from the ferrocyanide. The chlorine must not be used in *excess*, otherwise the salt will be decomposed.

Properties. A red crystalline salt, permanent in the air, and soluble in water (1 in 4 at 60° F.)

It is decomposed by reducing agents.

Its re-actions are important :

1. It forms insoluble precipitates of characteristic color with many metallic salts in neutral or in feebly acid solutions; *e.g.*, an *orange* precipitate with zinc or silver; a *yellow*, with cadmium; a *green*, with nickel and copper; a *reddish brown*, with cobalt; a *brown*, with manganese; a *white*, with stannous salts, etc.

Excepting those of zinc and tin, the ferricyanides of the above metals are insoluble in dilute hydrochloric acid.

2. (α.) *With a ferric* or *persalt of iron* (that is, where the iron is really a hexad, although apparently trivalent, as in $(Fe_2)^{vi}Cl_6$, it gives *no* precipitate, but merely turns the solution a reddish brown color.

(β.) With *a ferrous* or *protosalt of iron* (that is, where the iron is bivalent, as in $Fe''Cl_2$) it gives a deep blue precipitate of *ferrous ferricyanide*, $Fe''_3Fe'''_2Cy_{12}+Aq$, which, when dried, constitutes "*Turnbull's blue.*"

[NOTE.—Potassic ferrocyanide forms a blue precipitate (Prussian blue) with ferric salts, but not with ferrous salts, potassic ferricyanide constituting the test for iron as a ferrous salt, in which case a blue precipitate is formed. To distinguish Prussian blue (ferric ferrocyanide, $Fe'''_4Fe''_3Cy_{18}$) from Turnbull's blue (ferrous ferricyanide, $Fe''_3Fe'''_2Cy_{12}$), add potassic hydrate :—with Prussian blue we obtain potassic ferrocyanide, and *ferric or red oxide of iron* (Fe_2O_3); whilst with Turnbull's blue we obtain potassic ferrocyanide and *magnetic* or *black oxide of iron* (Fe_3O_4).]

3. The ferricyanide is used in dyeing, a fabric being colored blue when boiled in a solution of the salt acidulated with acetic acid. Mixed with potassic hydrate it forms, as an oxidizing agent, a discharge for indigo. Thus :—

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$$2(K_3Fe'''Cy_6) + 2KHO = 2(K_4Fe''Cy_6) + O + H_2O.$$
Potassic ferricyanide + Potassic hydrate = Potassic ferrocyanide + Oxygen + Water.

The **Nitro-prussides.**—*Preparation.*—By the action of nitric acid on the ferro- or ferri-cyanides.

Hydro-nitroprussic acid, $H_2(NO)Fe''Cy_5$, has been prepared in a crystalline form.

The *sodic nitroprusside* ($Na_2(NO)Fe''Cy_5 + 2aq$) is the only salt of importance.

Preparation.—Potassic ferrocyanide is boiled with dilute nitric acid until a ferrous salt added to the solution gives a slate-colored precipitate. It is then boiled with an excess of sodic carbonate, and the solution filtered and crystallized.

Properties.—It is a brilliant red crystalline (rhombic) body. The soluble nitroprussides produce a purple color with a mere trace of an alkaline sulphide.

Constitution.—The nitroprussides may be regarded as containing a radical similar to ferrocyanogen ($Fe''Cy_6$), where one of the monatomic radical (NO) has replaced one of Cy.—($Fe''(NO)Cy_5$). This radical is diatomic, inasmuch as Cy_2 of the group remains unsaturated.

Ferric Ferrocyanide (Prussian Blue), $'Fe'''_4Fe''_3Cy_{18}$ or Fe_7Cy_{18} or $3Fe''Cy_2, 2'Fe'''_2Cy_6$, or $2(Fe_2)^{vi}Cy_6, 3Fe''Cy_2 + 18H_2O$).

History.—It was discovered about 1700. Its true nature was not at first understood. Macquer (1724) discovered that it was decomposed by an alkali, a residue being formed of red oxide of iron. Hence he supposed it must be a compound of oxide of iron with an acid, but which acid had a greater affinity for an alkali than it had for oxide of iron. This view was supported by the fact that when a salt of iron was added to the solution, prussian blue was re-formed. Scheele, in 1782, prepared the acid which he called prussic acid. Gay Lussac, in 1815, called prussian blue *prussiate of iron.*

Preparation.—(1.) By the action of potassic ferrocyanide on ferric salts.

$$3K_4Fe''Cy_6 + 2Fe_2Cl_6 = 'Fe'''_4Fe''_3Cy_{18} + 12KCl.$$
Potassic ferrocyanide + Ferric chloride = Ferric ferrocyanide + Potassic chloride.

[This precipitate forms what is commercially known as *soluble prussian blue,* the precipitate being soluble in pure water.]

(2.) By the action of a mixture of ferrous and ferric salts on potassic cyanide. (This constitutes the principle of Scheele's test for HCN. (*See* page 522.)

$$3Fe''Cl_2 + 2'Fe'''_3Cl_6 + 18KCy = 18KCl + 'Fe'''_4Fe''_3Cy_{18}.$$
Ferrous chloride + Ferric chloride + Potassic cyanide = Potassic chloride + Prussian blue.

(3.) By the action of oxidizing agents, such as air, nitric acid,

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chlorine, etc., on the light blue precipitate of potassic ferrous ferrocyanide (Everitt's white salt = $FeK_2,FeCy_6$) produced when ferrous salts are precipitated with potassic ferrocyanide.

(α.) $K_4Fe''Cy_6 + FeSO_4 = FeK_2FeCy_6 + K_2SO_4$.
Potassic ferrocyanide + Ferrous sulphate = Potassic ferrous ferrocyanide + Potassic sulphate.

(β.) $6(FeK_2,Fe''Cy_6) + 3O_2 = 3(K_4Fe''Cy_6) + Fe_2O_3 + 'Fe'''_4Fe''_3Cy_{18}$
Potassic ferrous ferrocyanide + Oxygen = Potassic ferrocyanide + Ferric oxide + Prussian blue.

[This process is ordinarily employed in the manufacture of prussian blue. The prussian blue made in this way, however, is not so pure as that prepared by process 1, the pigment being always more or less mixed with potassic-ferrous-ferricyanide ($Fe''K,Fe''Cy_6$), which has also a blue color, and which, it will be seen, differs only from the potassic-ferrous-ferrocyanide by the loss of one potassium atom.]

Properties.—Prussian blue is a hard, blue, and brittle substance, without taste or odor. It is largely used as a pigment, but its color is not of a very permanent nature. That prepared by process 1 is soluble in *pure* water; that by process 3 is insoluble. Heated in air, it burns freely, leaving a residue of Fe_2O_3. Heated without air, it gives off water, ammonic cyanide and ammonic carbonate, a carbide of iron remaining as a residue.

It is insoluble in *dilute acids*, except in a solution of oxalic acid, this solution forming blue ink; *strong sulphuric acid* turns it white, the color being restored on dilution with water. It is decomposed by strong nitric and hydrochloric acids. *Alkalies* and *alkaline carbonates* destroy the color, dissolving out a ferrocyanide, and leaving ferric oxide.

$'Fe'''_4Fe''_3Cy_{18} + 12KHO = 3K_4Fe''Cy_6 + 2Fe_2O_3 + 6H_2O$.
Prussian blue + Potassic hydrate = Potassic ferrocyanide + Ferric oxide + Water

[Thus the calico printer in forming a pattern on a fabric dyed with prussian blue, first discharges the color with an alkali, and then dissolves the ferric oxide formed with a dilute acid.]

(1.) *Tests for hydrocyanic acid and the cyanides.*

(α.) The odor of prussic acid.

(β.) *Argentic Nitrate;* gives with the acid a white precipitate of argentic cyanide (AgCy), insoluble in nitric acid, and soluble in alkaline cyanides; *almost* insoluble in ammonia. By this means, and also by its not being readily blackened on exposure, AgCy may be known from AgCl.

The argentic cyanide when heated evolves cyanogen, which burns with a rose-red flame, reduced silver only remaining in the tube.

(γ.) (Scheele's Test.) Add to the acid a few drops of a solution of

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potassic hydrate. Thus a potassic cyanide is formed ($HCN + KHO = KCN + H_2O$). Add to the KCy solution, a mixture of a *ferrous and ferric salt* (such as ferrous chloride and ferric chloride). The ferrous salt converts the cyanogen into ferro-cyanogen ($FeCy_6$), which combines with the iron of the ferric salt to form prussian blue ($18KCy + 3FeCl_2 + 2Fe_2Cl_6 = 18KCl + Fe_7Cy_{18}$). Now add *dilute sulphuric acid*, to re-dissolve any excess of the ferrous and ferric hydrates precipitated by the excess of potassic hydrate, the result being that pure prussian blue will be precipitated.

In dilute solutions the reaction is slow.

[Thus in hydrocyanic acid poisoning, a mixture of solutions of sulphate of iron, perchloride of iron, and potassic hydrate, constitutes the best antidote.]

(δ.) *Mercurous Nitrate;* a grey precipitate of metallic mercury, mercuric cyanide remaining in solution.

(ε.) Place some hydrocyanic acid, or a mixture of a cyanide and hydrochloric acid in a watch-glass. Invert over this a second watch-glass, moistened with a few drops of yellow ammonic sulphide, in such manner that the sulphide may be freely exposed to the vapor of the acid. Heat very gently to dryness. Thus an ammonic sulphocyanate (NH_4CNS) is formed:—

$$\underbrace{(NH_4)_2S + S_2}_{\text{Yellow ammonic sulphide}} + \underbrace{2HCy}_{\text{Hydrocyanic acid}} = \underbrace{2NH_4CyS}_{\text{Ammonic sulpho-cyanate}} + \underbrace{H_2S}_{\text{Sulphuretted hydrogen.}}$$

This residue, when touched with a ferric chloride solution, yields the blood-red color of ferric sulphocyanate.

Estimation of Hydrocyanic Acid.—1. Argentic nitrate is added to a known quantity of the solution, and the argentic cyanide formed collected and weighed.

100 grs. of AgCN = 19·4 grs. of CN, or
= 48·57 grs. of KCN.

2. Supersaturate a hydrocyanic acid solution with potash, and add a few drops of a solution of common salt. Add to this a nitrate of silver solution of known strength. Immediately that a permanent precipitate of AgCl occurs, it proves that all the HCN present in the solution has been converted into the soluble double salt KCyAgCy, the combination of the chlorine with the silver not occurring until this is complete. (Every 170 of $AgNO_3$ corresponds to 26 of cyanogen, and to 65·1 of KCy).

(2.) *Tests for the Ferrocyanides:*

Ferric salts; a blue ppt. of Prussian blue ($Fe'''_4\ Fe''_3Cy_{18}$).

Cupric salts; a red ppt. of cupric ferrocyanide ($Cu''_2Fe''\ Cy_6$).

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(3.) *Tests for the Ferricyanides :*
Ferric salts ; no ppt., but merely a reddish-brown solution formed.
Ferrous salts ; a blue ppt. of ferrous ferricyanide ($Fe''_3\ Fe'''_2\ Cy_{12}$).

(4.) *Tests for the Sulphocyanates* (Sulphocyanides) :
Ferric salts give a blood-red coloration from the formation of ferric sulphocyanate.

(5.) *Tests for the Nitroprussides :*
Alkaline sulphides give a purple color.

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CHAPTER XXII.

THE HYDROCARBONS.

SERIES OF HYDROCARBONS.—The Paraffins—Chloroform—The Olefines—Acetylene—Turpenes—Benzenes—Naphthalene—Anthracene—Formation of Alizarene.

SUPPLEMENT.—Paraffin and Petroleum—Turpentine—Volatile Oils—Camphors—Resins—Gum Resins—Oleo-Resins—Balsams—India Rubber—Gutta Percha.

THE HYDROCARBONS.

It will assist us if, before considering the hydrocarbons in detail, we note the following facts:—

1. Carbon is a *tetrad* element. When combined, therefore, with four monad atoms (as in CH_4), it is regarded as fully "saturated."

2. Although, however, the carbon in CH_4 is fully saturated, and is therefore incapable of further combination, nevertheless it can exchange one or more unit weights of its hydrogen for an equivalent quantity of some other element. Thus CH_4 can form CH_3Cl or CH_2Cl_2. These substitution compounds with the halogens are called *haloid derivatives*. Again, it can exchange its hydrogen for a monad group, such as $(CN)'$ $(NO_2)'$ $(NH_2)'$, etc., and thus form other derivatives, as $CH_3(CN)'$, etc.

3. Again, carbon has the property of uniting with itself (*duplication*). Whenever this occurs its atom-fixing power is increased by *at most* two monad units; thus—

1C	can unite with	4	unit weights of hydrogen, etc.,	to form	=	CH_4
2C	,, ,,	6	,, ,,	,,	=	C_2H_6
3C	,, ,,	8	,, ,,	,,	=	C_3H_8

This fact has been already represented graphically (*see* page 366).

A series where the members or terms of the series, as they are called, increase by a regular increment of CH_2, is called an *homologous series*. All the members of the series described above are fully saturated.

4. If a saturated hydrocarbon, as CH_4, be deprived of a molecule of hydrogen (H_2) a molecule is left (CH_2), which is "not saturated," and gives rise to a new homologous series, all the members of which are also non-saturated molecules; as follows:—

$$CH_2—C_2H_4—C_3H_6—C_4H_8, \text{ etc.}$$

These non-saturated hydrocarbons, however, are able to unite with other elements or compound radicals to form saturated compounds.

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5. By an *isologous* series, we imply a series in which the successive terms differ by H_2; thus the series

Ethane	... C_2H_6
Ethene (Ethelene)	... C_2H_4
Ethine (Acetylene)	... C_2H_2, etc.

constitute an isologous series.

6. Hydrocarbons of even equivalence (such as those with the formula C_nH_{2n+2}, as CH_4) may exist separately, whilst hydrocarbons of unequal equivalence (as CH_3 *methyl*) are incapable of existing in the free state, unless perhaps as double molecules, *i.e.* $\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.=C_2H_6$.

7. A hydrocarbon containing an even number of hydrogen atoms has been regarded as a hydride of a radical, containing an uneven number of hydrogen atoms. Thus methane (CH_4) may be regarded as a hydride of methyl ($CH_3.H$), ethane (C_2H_6) as a hydride of ethyl ($C_2H_5.H$), etc. The groups CH_3, C_2H_5, etc., are called either "hydrocarbon radicals," or, for reasons to be seen directly, "alcohol radicals."

It must, however, be remembered that there is no reason to believe that one of the hydrogens of the body CH_4, plays a different part in the compound to the other three. Experiment, indeed, is opposed to such a view.

8. (α.) An *alcohol* is a hydrocarbon in which one or more atoms of hydrogen have been replaced by one or more of the group (OH). An alcohol may be regarded as the organic analogue of a metallic hydrate, such as Na (OH). Thus

Methane CH_4 forms *methylic alcohol* $CH_3(OH)$;
Ethane C_2H_6 ,, *ethylic alcohol* $C_2H_5(OH)$; etc.

(β.) A *thio-alcohol* or *mercaptan* is, in like manner, the organic analogue of a metallic sulphydrate, as Na (SH); thus

Methylic sulphydrate $CH_3(SH)$; *Ethylic sulphydrate* C_2H_5 (SH).

9. (α.) An *oxygen ether* is a compound of hydrocarbon radicals and oxygen. It may, therefore, be regarded as an *alcoholic oxide* or *anhydride*. It will be remarked that the relationship of Na(OH) to Na_2O is an analogous relationship to that existing between an alcohol and an ether. Thus—

Sodic hydrate Na (OH) and *Sodic oxide* Na_2O correspond to
Ethylic alcohol C_2H_5 (OH) and *Ethylic ether* $(C_2H_5)_2O$.

(β.) In a sulphur (thio-ether) or selenium ether, the analogues of metallic sulphides or selenides, the O is replaced by S or by Se; as, *e.g.*, $(C_2H_5)_2S$.

10. An *aldehyde* is a hydrocarbon where the hydrogen is replaced by the group (COH)′. Thus:—

$CH_3.H$ *methane* yields CH_3 (COH) *acetic aldehyde.*

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It may be remarked here that an aldehyde is produced by the oxidation of an alcohol, and an acid by the oxidation of an aldehyde. Thus an aldehyde stands midway between an alcohol and an acid. Thus :—

$$\underset{\text{Ethylic alcohol}}{C_2H_6O} \quad — \quad \underset{\text{Acetic aldehyde}}{C_2H_4O} \quad — \quad \underset{\text{Acetic acid.}}{C_2H_4O_2}.$$

11. A *ketone* is an aldehyde where the H of the group COH in the aldehyde, is replaced by a monad hydrocarbon group. Thus :—

$$\underset{\text{Aldehyde}}{CH_3(COH)} \quad — \quad \underset{\text{Dimethyl ketone.}}{CH_3(CO(CH_3))}.$$

The ketones differ from the aldehydes in the products of their oxidation.

12. An *acid* is a hydrocarbon where the hydrogen is replaced by the group carboxyl (CO.OH)′. Thus :—

$$\underset{\text{Methane}}{CH_4} \; ; \; \underset{\text{Acetic acid}}{CH_3(COOH)} \quad — \quad \underset{\text{Benzene}}{C_6H_6} \; ; \; \underset{\text{Benzoic acid.}}{C_6H_5(COOH)}.$$

The acids may be regarded, therefore, as oxidized alcohols and aldehydes.

Series of Hydrocarbons.

We have to consider the following series of hydrocarbons :—

Series.	Formula of Series.	Examples.
I. Marsh gas (paraffins) ..	C_nH_{2n+2}	Methane CH_4 Ethane C_2H_6,
II. Olefines	C_nH_{2n}	Ethylene C_2H_4 Propylene C_3H_6,
III. Acetylene	C_nH_{2n-2}	Acetylene C_2H_2 Allylene C_3H_4,
IV. Terpenes	C_nH_{2n-4}	Quintone C_5H_6 Decone $C_{10}H_{16}$
V. Benzenes .. .. (Aromatic series.)	C_nH_{2n-6}	Benzene C_6H_6 Toluene C_7H_8
VI. Cinnamene	C_nH_{2n-8}	Cinnamene C_8H_8 Allylbenzene C_9H_{10}
VII.	C_nH_{2n-10}	Acetenylbenzene C_8H_6
VIII. Naphthalene	C_nH_{2n-12}	Naphthalene $C_{10}H_8$
IX.	C_nH_{2n-14}	Diphenyl $C_{12}H_{10}$
X. Anthracene	C_nH_{2n-18}	Anthracene $C_{14}H_{10}$
XI.	C_nH_{2n-16}	Stilbene $C_{14}H_{12}$
XII.	C_nH_{2n-22}	Diacetenyl-benzene $C_{16}H_{10}$
XIII. Chrysene	C_nH_{2n-24}	Chrysene $C_{18}H_{12}$
XIV.	C_nH_{2n-26}	
XV.	C_nH_{2n-32}	Tetraphenylethylene $C_{26}H_{20}$

Respecting these series we would note generally that—

1. The 2nd and 3rd series (viz., the olefine and acetylene series) may be obtained from the 1st series (the paraffins) by similar operations. Further we note that the paraffins do not form additive

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compounds with the haloids, but that the 2nd and 3rd series do, whereby they are rendered compounds of a similar constitution to the paraffins. Thus :—

C_2H_2	forms	$C_2H_2Cl_4$	{ a substitution derivative of }	C_2H_6
Acetylene		Tetrachlorethane		Ethane.

2. The paraffins are in all respects a singularly inert class of bodies.

3. The 1st, 2nd, and 3rd series do not form nitro-derivatives or sulphonic acids.

4. The "terpenes" (Series IV.) are a very stable group. They have a peculiar action on polarized light, and combine readily with the haloids, but they yield neither nitro derivatives nor sulphonic acids.

5. The benzenes (Series V.), or aromatic series as they have been called, and with them Series VIII. and X., form additive compounds with difficulty, but substitution derivatives with ease, these latter being stable bodies, and not decomposed in some cases even by fusion with potassic hydrate. The benzenes form nitro-compounds and sulphonic acids by their direct union with nitric and sulphuric acids, by which they may be distinguished from all the preceding, but not from the succeeding series.

6. The naphthalene, anthracene, chrysene and pyrene series of hydrocarbons, form by oxidation "quinones," that is, bodies where two units of hydrogen are replaced by two units of oxygen.

Marsh Gas Series, or Paraffins.

SERIES I.—*Formula* C_nH_{2n+2}.

NAME.	Formula.	Boiling point. F.	Boiling point. C.	Sp. Gr. at deg. Cent.	Remarks.
Methane ..	CH_4				*See* page 228.
Ethane ..	C_2H_6				*Ethylic hydride* $C_2H_5.H$.
Propane ..	C_3H_8				
Tetrane ..	C_4H_{10}	33·8°	1°	·600 at 0°	*Diethyl* $(C_2H_5)_2$.
Pentane ..	C_5H_{12}	100·4°	38°	·628 at 17°	
Hexane ..	C_6H_{14}	158·0°	70°	·669 at 16°	
Heptane ..	C_7H_{16}	210·2°	99°	·699 at 15°	
Octane ..	C_8H_{18}	255·2°	124°	·726 at 15°	*Dibutyl* $(C_4H_9)_2$.
Nonane ..	C_9H_{20}	298·4°	148°	·728 at 13°	
Decane ..	$C_{10}H_{22}$	334·4°	168°	·739 at 13°	
Undecane ..	$C_{11}H_{24}$	363·2°	184°	·765 at 16°	
Dodecane ..	$C_{12}H_{26}$	395·6°	202°	·774 at 17°	
Tridecane ..	$C_{13}H_{28}$	424·4°	218°	·792 at 20°	
Tetradecane	$C_{14}H_{30}$	464·0°	240°	—	
Pentadecane	$C_{15}H_{32}$	505·6°	262°	·825 at 16°	
Hexdecane..	$C_{16}H_{34}$	532·4°	278°		Solid—melts at 69·8° F. (21° C.)

The above table represents the gravities and boiling points of

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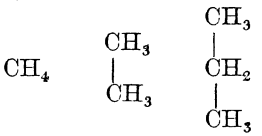
the normal primary paraffins. Several isomeric modifications of many of these bodies have been prepared, but not of the first three members of the series, viz., methane, ethane or propane. These isomers are prepared differently, have different gravities and boiling points, and exhibit different reactions. It is customary and convenient to express these varieties by different formulæ, although such expressions must be regarded as merely theoretical, and not in any sense representations of actual molecular construction.

Thus the first three terms of the series have no isomers, and however prepared, exhibit the same chemical and physical properties. They may be represented thus :—

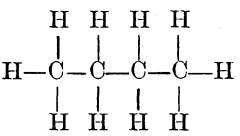


Methane. Ethane. Propane.

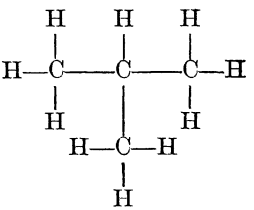
These, indeed, are the only ways in which it is possible to group the carbon atoms of these bodies. The fourth term C_4H_{10} is derived from the third term by the replacement of one hydrogen atom by the group CH_3. But this displacement of hydrogen may occur in one of two places ; *i.e.*, either in one of the end CH_3 groups, or in the centre CH_2 group ; that is in one case, none of the carbon atoms may be united with more than *two* carbon atoms, whilst in the second case one of the carbon atoms may be directly combined with *three* carbon atoms. Thus it may be represented as—

(1.) $(CH_3.CH_2.CH_2.CH_3)$, or as (2.) $(CH_3.CH(CH_3).CH_3)$.

We may express these two forms graphically thus—



No. 1.



No. 2.

Or again we may have such isomeric compounds as the following :—

$CH_3.CH_2.CH_2.CH_2(OH)$	=	Normal butylic alcohol.
$CH(CH_3)_2.CH_2(OH)$	=	Iso-primary do.
$C(CH_3)(C_2H_5)H.OH$	=	Secondary do.
$C(CH_3)_3(OH)$	=	Tertiary do.

It has been shown that all these various isomers (and it is evident that the number of isomers will increase with the advance of the series) may be represented under four heads :—

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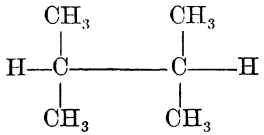
(1.) *Where each carbon atom is at most associated with two carbon atoms* (No. 1 as figured on last page).

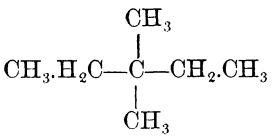
(2.) *Where one carbon atom is associated with three carbon atoms* (No. 2 as figured on last page).

(3.) *Where such group (i.e., of one carbon atom being associated with three carbon atoms) occurs twice in a molecule, as e. g.—*



No. 3.

(4.) *Where one carbon atom is associated with four other carbon atoms, as e. g., in—*



No. 4.

Similarly it must be noted that various isomers of the derivatives of the paraffins also result from the displacement taking place in different groups. Thus—

$CH_3.CH_2.CH_2I$ = propyliodide (*α–iodopropane*).
$CH_3.CHI.CH_3$ = iso-propyliodide (*β–iodopropane*).

Preparation of the Paraffins.—(*General.*)—1. *From the alcohols of the* $C_nH_{2n+1}OH$ *Series.* These are first (α) converted into monochlorinated, etc., paraffins by the action of a haloid acid, and afterwards (β) submitted to the action of nascent hydrogen. These reactions will be noted in the preparation of ethane;

(α.) $C_2H_5(OH) + HCl = (C_2H_5)Cl + H_2O.$
Ethylic alcohol + Hydrochloric acid = Ethylic chloride + Water.

(β.) $(C_2H_5)Cl + H_2 = C_2H_6 + HCl.$
Ethylic chloride + Hydrogen = Ethane + Hydrochloric acid.

2. By the action on the alcoholic iodides, either (α), of zinc and water, or (β), of zinc alone and heat, in closed vessels.

(α.) $2C_2H_5I + Zn_2 + H_2O = ZnH_2O_2 + ZnI_2 + 2C_2H_6.$
Ethylic iodide + Zinc + Water = Zincic hydrate + Zincic iodide + Ethane.

(β.) $2C_2H_5I + Zn = ZnI_2 + C_4H_{10}.$
Ethylic iodide + Zinc = Zincic iodide + Tetrane.

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3. *From the acetic series of acids* by electrolysis.

$$\underset{\text{Acetic acid}}{2C_2H_4O_2} = \overbrace{\underset{\text{Ethane}}{C_2H_6} + \underset{\text{Carbonic anhydride}}{2CO_2}}^{+} + \overbrace{\underset{\text{Hydrogen.}}{H_2}}^{-}.$$

4. *From the acids* (α) *of the acetic series, and* (β) *of the succinic series,* by the action of alkalies on their alkaline salts.

(α.) $KC_2H_3O_2 + KHO = K_2CO_3 + CH_4$.

Potassic acetate + Potassic hydrate = Potassic carbonate + Methane.

(β.) $K_2C_8H_{12}O_4 + 2KHO = 2K_2CO_3 + C_6H_{14}$.

Potassic suberate + Potassic hydrate = Potassic carbonate + Hexane.

General Properties.—(α.) *Physical.* The viscidity of the paraffins increases with their molecular weight, the members of the series becoming gradually less volatile and of higher gravity. Thus the first three terms are gaseous, those next in order are liquid, whilst the final terms are solid.

(β.) *Chemical.* Chlorine, and bromine to a less extent, act directly on the paraffins under the influence of sunlight, to form substitution products, which may be partial or complete. Iodine forms no such compounds directly, but it forms them indirectly. Thus it forms *iodoform* (CHI_3) by its action, in the presence of potassic hydrate, on various organic substances, such as sugar, alcohol, etc.

When chlorine acts on the normal primary paraffins, it forms simultaneously two isomeric derivatives, differing in their boiling points and in their specific gravities, and convertible respectively into a normal primary and a normal secondary monohydric alcohol. One or two illustrations will suffice :—

	Boiling pt. of Derivative.				Specific Gravity, at ° C.	
	(α.)		(β.)			
	° F.	° C.	° F.	° C.	(α.)	(β.)
CH_3Cl						
C_2H_5Cl	54·5	12·5			920 at 0°	
C_3H_7Cl	115·7	46·5	102·2	39	915	874 at 10°
C_4H_9Cl	171·5	77·5	158·0	70	907	895 at 0°
$C_5H_{11}Cl$	223·7	106·5	231·8	111	901	886 at 0°

With nitric acid the higher paraffins form directly nitro-compounds, whilst on the lower terms of the series, nitric acid has no such action, although nitro-compounds may be produced by indirect means.

Some of the more important substitution derivatives of the paraffins are stated in the following table :—

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Name.	Formula.	Preparation and Properties.
Methylic chloride .. .. (Monochloromethane)	CH_3Cl	*Preparation.*—(1.) By the action of Cl on CH_4 in diffused light. (2.) By the action of HCl gas on methylic alcohol. *Properties.*—A colorless gas, condensing at —4° F. (—20° C.).
Methylene chloride .. (Dichloromethane)	CH_2Cl_2	*Preparation.*—By the action of Cl on CH_3Cl in sunshine. *Properties.*—A colorless liquid; specific gravity, 1·36; boils at 107·6° F. (42° C.).
Chloroform .. .. .. (Trichloromethane)	$CHCl_3$	*See* below.
Carbonic Tetrachloride. (Tetrachloromethane)	CCl_4	*Preparation.*—(1.) By the action of chlorine on chloroform in sunlight. (2.) By the action of Cl on warm CS_2. *Properties.*—A colorless liquid; specific gravity, 1·6; boils at 172·4° F. (78° C.). By the action of nascent hydrogen it may be successively reduced to CH_4.
Iodoform .. .. .. (Triiodomethane)	CHI_3	*Preparation.*—By the action of iodine on alcohol, etc., in the presence of potassic hydrate. *Properties.*—A yellow crystalline body, soluble in alcohol and in ether. It forms cyanoform, $2CH(CN)_3$, when heated with mercuric cyanide.
Nitro-methane	$CH_3(NO_2)$	*Preparation.*—By the action of argentic nitrate on methylic iodide ($CH_3I+AgNO_2=AgI+CH_3NO_2$). *Properties.*—An oily liquid; boils at 210·2° F. (99° C.). Forms with NaHO the derivative $CH_2Na(NO_2)$.
Nitro-ethane..	$C_2H_5(NO_2)$	*Preparation.*—By the action of argentic nitrate on ethylic iodide. *Properties.*—A colorless liquid; boils at 235·4° F. (113° C.). By the action of nascent hydrogen, forms *ethylamine*.
Cyano-ethane or Ethyl cyanide	$C_2H_5(CN)$	When methyl or ethyl iodide is heated with argentic cyanide, two isomeric ethyl or methyl liquid compounds are formed:— *Ethyl compounds* (1.) boils at 191·3° F. (88·5° C.); no odor. „ (2.) boils at 174·2° F. (79° C.); intolerable odor.
Cyanomethane or Methyl cyanide	$CH_3(CN)$	*Methyl compounds* (1.) boils at 170·6° F. (77° C.); not acted on by acids. „ (2.) boils at 131° F. (55° C.); decomposed by acids.

Trichloromethane (Chloroform). *Terchloride of formyle; methenyl chloride; dichlorinated methylic chloride* ($CHCl_3$).

Molecular weight, 119·5. *Specific gravity*, 1·48. *Boils at* 141·8° F. (61·0° C.). *Vapor density* (*air*=1) 4·20.

Preparation.—(1.) By the action of chlorine on methane.

(2). (Commercial method.) By distilling together 1 part of alcohol (wood spirit being sometimes employed), 6 parts of chloride of lime, and 24 parts of water. The distillate consists of water and chloroform,

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which, on standing, separates into two layers, the water being above, and the chloroform below. The exact reaction is doubtful. Probably (α) chloral is formed in the first stage, and (β) in the next stage is decomposed by the calcic hydrate; thus—

(α.)	$C_2H_5(OH)$	+	$4Cl_2$	=	$5HCl$	+ CCl_3COH.
	Alcohol	+	Chlorine	=	Hydrochloric acid	+ Chloral.
(β.)	$2CCl_3COH$	+	CaH_2O_2	=	$Ca''(CHO_2)_2$	+ $2CHCl_3$.
	Chloral	+	Calcic hydrate	=	Calcic formate	+ Chloroform.

The chloroform is afterwards purified from certain oils that distil over along with it, by being shaken up with oil of vitriol, on which the chloroform floats. It is then drawn off from the acid and again distilled.

Properties.—(α.) *Physical.* A colorless liquid, having a fragant odor and a sweet taste; specific gravity, 1·48. It is insoluble in water.

(β.) *Chemical.* Chloroform burns with difficulty with a greenish flame. Sulphuric acid has no action upon it; boiled with nitric acid it forms *chloropicrin* (*nitrotrichloromethane*) $[C(NO_2)Cl_3]$, a colorless liquid, having a specific gravity of 1·6, and boiling at 233·6° F. (112° C.). Boiled with a solution of potassic hydrate it forms potassic chloride and formate ($CHCl_3+4KHO=3KCl+CHO(OK)+2H_2O$). When heated with potassium amalgam, *acetylene* (C_2H_2) is set free. Distilled in a current of chlorine, it forms CCl_4.

Uses.—As an anæsthetic. For dissolving caoutchouc, and for extracting the alkaloids from organic matters.

(*See* SUPPLEMENTARY CHAPTER.)

The Olefines.

SERIES II.—*Formula* C_nH_{2n}.

The following hydrocarbons of this series have been obtained :—

	Formula	Melting point.		Boiling point.		
		° F.	° C.	° F.	° C.	
Ethylene (ethene) ..	C_2H_4					See page 229.
Propylene (propene)	C_3H_6			—0·4	—18	
Butylene (quartene)	C_4H_8			33·8	1	
Amylene (quintene)	C_5H_{10}			95	35	A colorless liquid.
Hexylene (sextene)	C_6H_{12}			149	65	
Heptylene (septene)	C_7H_{14}			204·8	96	
Octylene (octene) ..	C_8H_{16}			248	120	
Nonylene (nonene)	C_9H_{18}			284	140	
Diamylene (decene)	$C_{10}H_{20}$			320	160	
Triamylene	$C_{15}H_{30}$			482	250	
Cetene (sexdecene)	$C_{16}H_{32}$			527	275	
Tetramylene	$C_{20}H_{40}$			752	400	
Cerotene	$C_{27}H_{54}$	134·6	57		(?)	
Melene	$C_{30}H_{60}$	143·6	62	707	375 (?)	

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Preparation of the Olefines (*General.*)—1. From the *alcohols* of series $C_nH_{2n+1}OH$. By abstracting the elements of water by dehydrating reagents, such as sulphuric acid. Thus:—

$C_2H_5.OH$	=	C_2H_4	+	H_2O.
Ethylic alcohol	=	Ethylene	+	Water.

2. From the *paraffins*. (α.) By the action of lime or potassic hydrate on their mono-haloid derivatives. Thus:—

C_4H_9I	+	KHO	=	C_4H_8	+	KI	+	H_2O.
Iodotetrane	+	Potassic hydrate	=	Butylene	+	Potassic iodide	+	Water.

(β.) By the action of sodium on a mixture of a mon-iodo-paraffin and a mon-iodo-olefine.

(γ.) By the decomposition of a mon-iodo-paraffin. At the moment that the monad radical is set free, its transformation, by the action of zinc or sodium, into the dyad radical and the hydride of the monad radical, may be accomplished. This is seen in the formation of ethylene:—

$2C_2H_5I$	+	Zn	=	C_2H_4	+	ZnI_2	+	$C_2H_5.H$.
Ethylic iodide	+	Zinc	=	Ethylene	+	Zincic iodide	+	Ethylic hydride.

(δ.) By the action of a mon-iodo-paraffin on a sodium compound of the same radical. Thus:—

C_2H_5I	+	C_2H_5Na	=	C_2H_4	+	NaI	+	C_2H_5H.
Ethylic iodide	+	Sodium ethyl	=	Ethylene	+	Sodic iodide	+	Ethylic hydride.

3. From *other simpler hydrocarbons* by direct synthesis. Thus:—

(α.)	C_2H_2	+	H_2	=	C_2H_4.
	Acetylene	+	Hydrogen	=	Ethylene.

(β.)	$2CH_4$	+	CO	=	C_3H_6	+	H_2O.
	Methane	+	Carbonic oxide	=	Propylene	+	Water.

4. From acids of the $C_nH_{2n}(CO.OH)_2$ series, by electrolysis.

Properties (*General.*)—(α.) *Physical.* The lower members of this series are gaseous; the higher are solid; the intermediate ones are liquid.

(β.) *Chemical.* The olefines are dyad radicals. Thus they unite with two atoms of the haloids (as $C_2H_4Br_2$), or with one of oxygen (as C_2H_4O). They unite directly with the haloids, forming compounds which are decomposed by an alcoholic solution of potassic hydrate. Thus:—

$C_2H_4Cl_2$	+	KHO	=	KCl	+	H_2O	+	C_2H_3Cl.
Ethylene dichloride	+	Potassic hydrate	=	Potassic chloride	+	Water	+	Chlor-ethylene.

The compound C_2H_3Cl may be made to combine with Cl_2 to form the compound $C_2H_3Cl_3$. When this is decomposed with alcoholic potash,

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it forms the compound $C_2H_2Cl_2$. These operations may be repeated until C_2Cl_4 is formed, which body will also combine with Cl_2 to form the solid "per substituted" paraffin, C_2Cl_6.

By the action of alcoholic potash on a monochlorinated (or monobrominated) olefine, a hydrocarbon of the series C_nH_{2n-2} is formed. Thus:—

C_2H_3Br	+	KHO	=	KBr	+	H_2O	+	C_2H_2.
Bromethylene	+	Potassic hydrate	=	Potassic bromide	+	Water	+	Acetylene.

With *strong sulphuric acid*, certain of the olefines form ethereal salts, or, as they are called, acid ethers of sulphuric acid (as $C_2H_4+H_2SO_4=C_2H_5.HSO_4$). These, when heated with water, are decomposed into sulphuric acid and the mon-atomic alcohol corresponding to the olefine (thus $C_2H_5.HSO_4+H_2O=H_2SO_4+C_2H_5(OH)$). With *fuming sulphuric acid*, such olefines form sulpho-acids (not acid ethereal salts), which sulpho-acids are not decomposed by water.

A paraffin cannot be formed directly from an olefine by the action of nascent hydrogen; nevertheless, such a change may be effected indirectly. Thus by heating ethylene iodide ($C_2H_4I_2$) in closed tubes for some hours with water, *ethane* (C_2H_6) is formed; this conversion being due to the hydrogen, set free from the decomposition of one portion of the ethylene iodide (α), acting on a second and undecomposed portion (β). Thus:—

(α.)	$C_2H_4I_2$	+	$4H_2O$	=	$6H_2$	+	$2CO_2$	+	I_2.
	Ethylene iodide	+	Water	=	Hydrogen	+	Carbonic anhydride	+	Iodine.

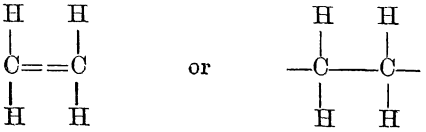
(β.)	$C_2H_4I_2$	+	H_2	=	C_2H_6	+	I_2.
	Ethylene iodide	+	Hydrogen	=	Ethane	+	Iodine.

The olefines form monochlorinated monohydric alcohols with hypochlorous acid (α), which, by the action of nascent hydrogen may be converted into the corresponding alcohols (β). Thus—

(α.) $C_2H_4 + ClOH = C_2H_4Cl(OH)$.

(β.) $C_2H_4Cl(OH) + H_2 = C_2H_5(OH) + HCl$.

Lastly, the olefines may exist either as saturated hydrocarbons or as dyad radicals, the difference depending on the linking of the carbon particles. Thus we may represent ethylene, either as



Saturated or as a dyad radical.

Acetylene Series.

SERIES III.—*Formula* C_nH_{2n-2}.

This includes the following bodies, isomeric modifications of most of which are known:—

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NAME.	Formula.	Boiling point. F.	Boiling point. C.
Acetylene (ethine)	C_2H_2		
Allylene (propine)	C_3H_4		
Crotonylene (quartine)	C_4H_6	64·4°	18·0°
Valerylene (quintine)	C_5H_8	113·0°	45·0°
Diallyl (sextine)	C_6H_{10}	136·4°	58·0°
Rutylene (decine)	$C_{10}H_{18}$	302·0°	150°

Preparation of the Acetylene Series (*General*).—1. *From the olefines.*—By acting on a mono haloid derivative, either with alcoholic potash, or with sodic ethylate, at a temperature of 302° F. (150° C.)

(α.) $C_2H_3Br + KHO = KBr + H_2O + C_2H_2$.

(β.) $C_2H_3Br + C_2H_5NaO = NaBr + C_2H_5(OH) + C_2H_2$.

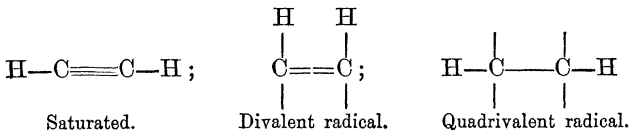
2. *From the acids of the maleic series* [$C_nH_{2n-2}(COOH)_2$], by electrolysis:—

$C_4H_4O_4 = C_2H_2 + 2CO_2 + H_2$.

Fumaric acid = Acetylene + Carbonic anhydride + Hydrogen.

Properties.—(α.) *Physical.*—Acetylene and allylene are gases; the rest are liquids.

(β.) *Chemical.*—The acetylene series may either exist in a free state, or they may act as divalent or quadrivalent radicals, thus—



Saturated. Divalent radical. Quadrivalent radical.

Thus C_2H_2 can combine with the haloids to form $C_2H_2Br_2$ or $C_2H_2Br_4$.

Turpene Series.

SERIES IV.—*Formula* C_nH_{2n-4}.

Of this series two terms only have been prepared synthetically.

	Formula.	Boiling point. F.	Boiling point. C.	
Quintone (valylene) ..	C_5H_6	140°	60°	Prepared by the action of potassic hydrate on valerylene dibromide ($C_5H_8Br_2$) and rutylene dibromide ($C_{10}H_{18}Br$) respectively.
Decone	$C_{10}H_{16}$	320°	160°	

(*See* SUPPLEMENTARY CHAPTER.)

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The Aromatic Series—The Benzenes.

Series V.—*Formula* C_nH_{2n-6}.

This includes :—

		Formula.	Boiling point. F.°	Boiling point. C.°	
C_6H_6	Benzene	C_6H_6	176·9	80·5	An isomer is known called *Dipropargyl.*
C_7H_8	Toluene (methylbenzene) ..	$C_6H_5.CH_3$	230·0	110	
C_8H_{10}	Xylene (ethylbenzene) ..	$C_6H_5(C_2H_5)$	275·0	135	*Xylene* of coal tar oil is principally metaxylene. By oxidation it yields *metatoluic acid.*
	Paraxylene } Dimethyl-	$C_6H_4(CH_3)_2$	276·8	136	
	Metaxylene } benzenes	$C_6H_4(CH_3)_2$	280·4	138	
	Orthoxylene }	$C_6H_4(CH_3)_2$	285·8	141	
C_9H_{12}	Propylbenzene	$C_6H_5(C_3H_7)$ (*a.*)	314·6	157	*Cumene* (mesitylene of coal tar oil) may be obtained by heating acetone with sulphuric acid :— $3C_3H_6O=C_9H_{12}+3H_2O.$
	Isopropylbenzene	$C_6H_5(C_3H_7)$ (*β.*)	303·8	151	
	Ethelmethylbenzene ..	$C_6H_4(CH_3)(C_2H_5)$	320·0	160	
	Mesitylene } Trimethyl-	$C_6H_3(CH_3)_3$	325·4	163	
	Pseudocumene } benzenes	$C_6H_3(CH_3)_3$	330·8	166	
$C_{10}H_{14}$	Isobutylbenzene	$C_6H_5(C_4H_9)$ (*β.*)	320·0	160	*Cymene* has been obtained synthetically in all its forms except modification (*a.*).
	Propylmethylbenzene ..	$C_6H_4(CH_3)(C_3H_7)$ (*a.*)	354·2	179	
	Isopropylmethylbenzene ..	$C_6H_4(CH_3)(C_3H_7)$ (*β.*)	348·8	176	
	Diethylbenzene	$C_6H_4(C_2H_5)_2$	354·2	179	
	Ethyldimethylbenzene ..	$C_6H_3(C_2H_5)(CH_3)_2$	363·2	184	
	Tetramethylbenzene ..	$C_6H_2(CH_3)_4$	374·0	190	
$C_{11}H_{16}$	Isoamylbenzene	$C_6H_5(C_5H_{11})$ (*β.*)	379·4	193	
	Isopropyldimethylbenzene	$C_6H_3(CH_3)_2(C_3H_7)$ (*β.*)	370·4	188	
	Diethylmethylbenzene ..	$C_6H_3(CH_3)(C_2H_5)_2$	352·4	178	
$C_{12}H_{18}$	Isoamylmethylbenzene ..	$C_6H_4(CH_3)(C_5H_{11})$ (*β.*)	415·4	213	
$C_{13}H_{20}$	Isoamyldimethylbenzene ..	$C_6H_3(CH_3)_2(C_5H_{11})$ (*β.*)	451·4	233	

General Preparation of the Benzenes.—(1.) The benzenes may be obtained from coal tar.

(2.) By the action of sodium on a mixture of a moniodated paraffin with a brominated derivative either of benzene, or of an homologous hydrocarbon :—

$$C_nH_{2n+1}I+C_nH_{2n-7}Br+Na_2=C_nH_{2n-7}.C_nH_{2n+1}+NaI+NaBr.$$

Properties (*General*).—This group, most of the members of which may be obtained from coal tar naphtha, and may also be *prepared* synthetically, is called *the aromatic group*, on account of the fragrant odor of many of the series. As a class, the benzenes are very stable bodies, and are remarkable for the numerous isomers and metamers that the various terms afford, toluene standing almost alone in the series in having no isomers.

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The aromatic series act as saturated molecules, forming substitution rather than additive compounds, differing in this respect from the former groups we have considered, the tendency of which was rather to form additive than substitution compounds.

The constitution of these hydrocarbons is important. They all contain a group of 6 carbon atoms; 24 (6×4), therefore, is the total combining or atom-fixing power of the 6 atoms. But 18 of this 24 power is occupied by the combination of the carbon atoms with each other, leaving only a power of 6 to be filled up to form a fully saturated molecule. Thus C_6H_6 may be regarded as a fully saturated hydrocarbon. This is shown in Fig. 1:—

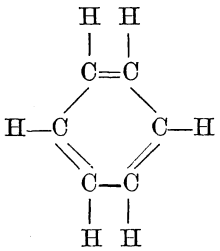

Fig. 1.

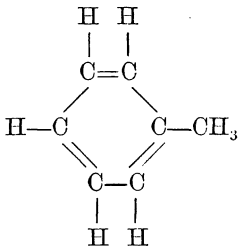

Fig. 2.

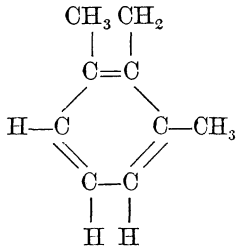

Fig. 3.

It will be seen how other bodies may be derived from this compound by the substitution of more or less complicated molecules in the place of the hydrogen, as in Fig. 2, which represents toluene, or, as in Fig. 3, which represents mesitylene (cumene).

The table on page 537 exhibits some of the numerous isomers of this series. We shall note isomeric compounds made up of *the same* groups, as *e.g.*, 3 dimethyl benzenes, $C_6H_4(CH_3)_2$, as well as isomeric compounds made up of *different* groups, such as *ethylbenzene* $(C_6H_5)(C_2H_5)$ and *dimethylbenzene* $(C_6H_4)(CH_3)_2$. The nature of these hydrocarbons is to be specially inferred *by their behaviour on oxidation*, as when treated with dilute nitric or chromic acids. The following facts on this point must be noted:—

(1.) *Benzene* forms no oxidation products that contain 6 carbon atoms. It may be burnt and form H_2O and CO_2. It may also be made to form benzoic acid $(C_7H_6O_2)$ or phthalic acid $(C_8H_6O_4)$.

(2.) All the derivatives of benzene formed by the replacement of one atom of hydrogen by the group C_nH_{2n+1}, such as *methylbenzene* $C_6H_5(CH_3)$, *propylbenzene*, $C_6H_5(C_3H_7)$, *butylbenzene*, $C_6H_5(C_4H_9)$, *amylbenzene*, $C_6H_5(C_5H_{11})$, etc., yield, by oxidation, one and the same acid, *viz.*, *benzoic acid* $(C_7H_6O_2)$.

(3.) The derivatives formed by the replacement of H_2 by two groups of the formula C_nH_{2n+1}, such as *dimethylbenzene*, $C_6H_4(CH_3)_2$ or *diethylbenzene*, $(C_6H_4(C_2H_5)_2$, produce by oxidation, in the first instance an acid of the benzoic acid series, whilst they all finally yield the same acid, *viz.*, *terephthalic acid*, $C_6H_4(COOH)_2$.

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(4.) The derivatives formed by the replacement of H_3 by 3 groups of the formula C_nH_{n+1}, such as *trimethylbenzene*, $C_6H_3(CH_3)_3$, etc., yield on oxidation as their final product *mesitic acid*, $C_6H_3(COOH)_3$.

The molecular constitution of these bodies may be further inferred by their synthetical formation. Thus *methylbenzene* or *toluene* $C_6H_5(CH_3)=(C_7H_8)$ is obtained by the action of sodium on a mixture of *methylic* iodide and bromobenzene; *ethylbenzene* or *xylene*, $C_6H_5(C_2H_5)=(C_8H_{10})$ is obtained by the action of sodium on a mixture of *ethylic* iodide and bromobenzene; whilst *dimethylbenzene*, $C_6H_4(CH_3)_2=(C_8H_{10})$, an isomer of xylene, is formed by the action of sodium on iodomethane and dibromobenzene.

Chlorine and bromine form substitution and additive compounds with benzene *in the presence of iodine*. The iodine acts in such cases as the carrier of chlorine, that is, the chloride of iodine forms moniodobenzene with the benzene, and this, by the action of a further portion of iodine chloride, is converted into chlorobenzene. Thus—

(α.) $C_6H_6 + ClI = C_6H_5I + HCl.$

Benzene + Iodine chloride = Iodobenzene + Hydrochloric acid.

(β.) $C_6H_5I + ClI = C_6H_5Cl + I_2.$

Iodobenzene + Iodine chloride = Chlorobenzene + Iodine.

Iodobenzenes may be formed by the action of iodine on benzene *in the presence of iodic acid*. The iodic acid decomposes the hydriodic acid as soon as formed. If iodic acid was not added, the hydriodic acid would decompose the iodo derivative, by withdrawing iodine from it and replacing it by hydrogen. The following equations will explain this:—

(1.) *Without iodic acid;* $C_6H_5I+HI=C_6H_6+I_2$.

(2.) *With iodic acid;* $C_6H_5I+5HI+HIO_3=C_6H_5I+3H_2O+3I_2$.

On toluene in the cold, chlorine forms the stable compound *chlorotoluene* (C_7H_7Cl), which is unacted upon, either by nascent hydrogen or by fusion with alkalies. *On boiling toluene*, chlorine forms *benzylic chloride* (C_7H_7Cl), a body having the same composition as chlorotoluene, but differing from it, in that nascent hydrogen changes it to toluene, and alkalies readily decompose it. *On boiling toluene, however, in the presence of iodine*, the stable body *chlorotoluene* is formed, which as we have said, is singularly unamenable to the action of ordinary reagents.

With strong nitric acid the benzenes form nitro derivatives [$C_6H_6+HNO_3=H_2O+C_6H_5(NO_2)$]. With sulphuric acid they form sulphonic acids [$C_6H_6+H_2SO_4=H_2O+C_6H_5(HSO_3)$]; and with hydriodic acid, aided by a continuous heat of 536° F. (280° C.) they are converted into the corresponding paraffins.

Benzene.—*Benzol; bicarburet of hydrogen; phenylic hydride* (C_6H_6). [*Molecular weight*, 78. *Molecular volume*, $\underline{|\,|}$. *Boils at* 176·9° F. (80·5° C.).]

Preparation.—(1.) By the action of heat on acetylene ($3C_2H_2=C_6H_6$).

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(2.) By the distillation (α) of benzoic acid with lime, or (β) by the action of heat only on benzoic acid :—

(α.) $C_6H_5(CO.OH) + CaH_2O_2 = CaCO_3 + H_2O + C_6H_6$.
Benzoic acid + Lime = Calcic Carbonate + Water + Benzene.

(β.) $C_6H_5(COOH) = CO_2 + C_6H_6$.
Benzoic acid = Carbonic anhydride + Benzene.

Its preparation from that portion of the coal tar boiling below 180° F. (82·2° C.), has been already referred to (page 500).

Properties.—(α.) *Physical.* A colorless, inflammable liquid of high refracting power, having an ethereal odor and a burning taste. Its Sp. Gr. at 0° C. is 0·899. It boils at 176·9° F. (80·5° C.), and solidifies at 41·9° F. (5·5° C.) to a white crystalline solid. It is insoluble in water, but is soluble in alcohol and in ether, and is a solvent for iodine, sulphur, phosphorus, fats, resins, etc. When its vapor is passed through a porcelain tube heated to bright redness, it is decomposed into the gases *hydrogen* and *acetylene* (C_2H_2), into the liquids *diphenyl* ($C_{12}H_{10}$) and *chrysene* ($C_{18}H_{12}$), and into an orange-colored solid called *benzerythrene*.

(β.) *Chemical.* With the haloids, benzene forms both additive and substitution compounds. As illustrations of the *additive compounds* that it forms, we have *benzene hexachloride* ($C_6H_6Cl_6$) and *benzene hexabromide* ($C_6H_6Br_6$), both of which are solid bodies, formed by the action of sunlight on a mixture of chlorine and benzene. As illustrations of *substitution compounds*, we have monochlorobenzene, C_6H_5Cl, and also the compounds $C_6H_4Cl_2$, $C_6H_3Cl_3$, etc.

Some of the benzene derivatives are stated in the following table :—

	Formula.	Boiling point.		Melting point.	
		° F.	° C.	° F.	° C.
Monochlorobenzene	C_6H_5Cl	276·8	136	—40	—40
Dichlorobenzene	$C_6H_4Cl_2$	339·8	171	+127·4	+53
Trichlorobenzene	$C_6H_3Cl_3$	402·8	206	62·6	17
Tetrachlorobenzene	$C_6H_2Cl_4$	464·0	240	282·2	139
Pentachlorobenzene	C_6HCl_5	521·6	272	185·0	85
Hexachlorobenzene	C_6Cl_6	618·8	326	438·8	226
Monobromobenzene	C_6H_5Br			302·0	150
Dibromobenzene	$C_6H_4Br_2$			417·2	214
Tribromobenzene	$C_6H_3Br_3$	527·0	275	111·2	44
Tetrabromobenzene	$C_6H_2Br_4$				
The iodobenzenes are similar to the above.					
Nitrobenzene .. .. (Artificial oil of almonds.)	$C_6H_5NO_2$				
Dinitrobenzene	$C_6H_4(NO_2)_2$				

The chlor-benzenes are formed by passing chlorine into a solution of iodine in benzene, the iodine acting as a carrier of the chlorine to the benzene.

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The benzene haloid derivatives are very stable bodies. Unlike the paraffin derivatives, they are unaffected by nascent hydrogen, or even by fusion with potassic hydrate. With hypochlorous acid, benzene forms the additive compound $C_6H_6(ClOH)_3$, which, by the action of water, forms a non-fermentable body called "phenose," having the same composition as grape-sugar. When this body is dissolved in fuming nitric acid, and water added to the solution, nitrobenzene ($C_6H_5NO_2$), or artificial essence of bitter almonds, separates, which, by the action of reducing agents, yields aniline.

Toluene.—*Methylbenzene* ($C_7H_8=C_6H_5.CH_3$. [*Molecular weight*, 92. *Boils at* 230° F. (110° C.). *Not solid at* —4° F. (—20° C.). *Specific gravity*, 0·881 at 41° F. (5° C.).]

Preparation.—(1.) From coal tar oil. (*See* page 497.) It is contained in that portion boiling between 212° and 248° F. (100° and 120° C.).

(2.) By the action of sodium on a mixture of bromobenzene and methyl iodide. Thus:—

C_6H_5Br	+	CH_3I	+	Na_2	=	NaBr	+	NaI	+	$C_6H_5.CH_3$.
Bromobenzene	+	Methyl iodide	+	Sodium	=	Sodic bromide	+	Sodic iodide	+	Toluene.

(3.) By the action of methane in a nascent state on benzene.

Properties.—A limpid liquid. Sp. Gr. 0·881 at 5° C. Boils at 230° F. (110° C.). Chemically, it behaves very like benzene, yielding benzoic acid when treated with oxidising agents.

Two isomeric derivatives are formed in almost every case by the action of reagents on toluene.

Series VI.—*Formula* C_nH_{2n-8} Series.

This includes:—

		Boiling point.		
		° F.	° C.	
Cinnamene.. .. (Styrolene)	C_8H_8	293	145	*Preparation.*—(1.) By passing the vapors of benzene and acetylene, or (2.) of benzene and ethylene, through a red-hot tube. (3.) By heating acetylene ($4C_2H_2=C_8H_8$). (4.) It is present in, and may be obtained from, liquid storax. *Properties.*—A colorless liquid. It does not solidify at —4° F. (—20° C.) Heated in closed tubes to 392° F. (200° C.) it is converted into a white solid *metacinnamene*, which yields, on distillation, liquid *cinnamene*.
Allylbenzene ..	C_9H_{10}	338	170	*Preparation.*—By the action of nascent hydrogen on cinnamic alcohol.
Phenylbutylene..	$C_{10}H_{12}$			*Preparation.*—By the action of sodium on a mixture of benzylic chloride and allylic iodide.

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SERIES VII.—*Formula* C_nH_{2n-10} Series.

This includes,

Acetenylbenzene (C_8H_6) a colorless liquid boiling at 282·2° F. (139° C.). It is prepared by the action of an alcoholic solution of potassic hydrate on cinnamene dibromide ($C_8H_8Br_2+2KHO=C_8H_6+2KBr+2H_2O$). Like acetylene it precipitates many metallic solutions.

The Naphthalene Series.

SERIES VIII.—*Formula* C_nH_{2n-12}.

This includes:—

		Boiling point.	
		° F.	° C.
Naphthalene	$C_{10}H_8$	413·6	212
Methyl naphthalene.. ..	$C_{10}H_{10} = C_{10}H_7(CH_3)$	447·8	231
Ethyl naphthalene	$C_{12}H_{12} = C_{10}H_7(C_2H_5)$	483·8	251

Naphthalene ($C_{10}H_8$).

Occurrence and Preparation.—(1.) Naphthalene is a bye-product in the preparation of coal gas. In distilling coal tar, the latter portion of the distillate contains a large quantity of naphthalene. It is produced whenever organic matter is distilled at a high temperature out of contact with air, or whenever the vapours of benzene, cinnamene, chrysene or anthracene are passed through a red-hot tube.

(2.) By passing the vapour of dibromophenylbutylene over red-hot lime ($C_{10}H_{12}Br_2=C_{10}H_8+H_2+2HBr$).

Properties.—(α). *Physical.*—A white solid body, crystallizing in brilliant scales. It has a faint narcissus-like odour. It melts at 176° F. (80° C.) and boils at 413·6° F. (212° C.) Its vapor density is 4·528. It is insoluble in cold water—slightly soluble in boiling water—very soluble in alcohol, in ether, in acetic acid, and in the volatile oils.

(β.) *Chemical.*—It burns in air with a red smoky flame. It forms with chlorine and with bromine both additive and substitution compounds, such as $C_{10}H_8Cl_4$ and $C_{10}H_7Cl$, etc. By oxidation it yields *dinaphthyl*, $C_{20}H_{14}$, and *phthalic acid* $C_8H_6O_4$. It is soluble in strong sulphuric acid, forming two isomeric *naphthalene-sulphonic acids*, $C_{10}H_7(HSO_3)$ both of which form soluble baric salts. Nitric acid

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converts it, first, into a crystalline solid *nitronaphthalene* $C_{10}H_7NO_2$, and finally into *tetranitronaphthalene* $C_{10}H_4(NO_2)_4$. With a solution of chromic anhydride in acetic acid, it forms *naphtho-quinone* $C_{10}H_6O_2$.

SERIES IX.—*Formula* C_nH_{2n-14} Series.

This includes :—

		Melting point.		Boiling Point.		
		° F.	° C.	° F.	° C.	
$C_{12}H_{10}$	Diphenyl.. .. .. (C_6H_5,C_6H_5)	140·0	60·0	464·0	240·0	*Preparation.*—By passing benzene through a red-hot tube ($2C_6H_6=C_{12}H_{10}+H_2$). By oxidation it forms *benzoic acid*. It sublimes at 140° F. (60° C.). It is contained in coal-tar, and distils over in that portion that boils between 518° and 572° F. (270° and 300° C.). By oxidation it forms *naphthalic acid*, which, when distilled with lime, yields *naphthalene*.
	Acenaphthene.. ..	203·0	95·0	514·4	268·0	
$C_{13}H_{12}$	Diphenyl methane.. (Benzyl benzene) (C_6H_5,CH_2,C_6H_5)	79·7	26·5	501·8	261·0	*Preparation.* — By the action of heat on a mixture of benzylic chloride and benzene ($C_6H_6+C_7H_7Cl=HCl+C_{13}H_{12}$). [The presence of a little zinc and copper facilitate the action.] By oxidation it yields *benzophenone* ($C_6H_5.CO.C_6H_5$).
$C_{14}H_{14}$	Ditolyl (α)	249·8	121·0			*Preparation.* — By the action of sodium on benzylic chloride. It is insoluble in water, but is soluble in alcohol and ether.
	„ (β) .. .. ($CH_3.C_6H_4.C_6H_4.CH_3$)	liquid				
	Dibenzyl.. .. .. ($C_6H_5.CH_2.CH_2.C_6H_5$)	125·6	52·0	543·2	284·0	
	Benzyltoluene ..	liquid		534·2	277·0	
$C_{15}H_{16}$	Benzyl ethylbenzene	liquid		561·2	294·0	
	Benzyl metaxylene .	liquid		563·0	295·0	
	Benzyl paraxylene..	liquid		561·2	294·0	

Excepting acenaphthene, all these bodies act as saturated molecules and form substitution but not additive compounds.

The Anthracene Series.

SERIES X.—*Formula* C_nH_{2n-18}.

This includes :—

		Melting point.		Boiling point.	
		° F.	° C.	° F.	° C.
Anthracene	$C_{14}H_{10}$	415·4	213	680	360
Dimethylanthracene	$C_{16}H_{14}$				

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Anthracene (*Paranaphthalene.*) ($H_{14}H_{10}$) *Molecular weight* 178. *Specific gravity* 1·147. Melts at 415·4° F. (213° C); boils at 680° F. (360° C.)

Preparation.—(1.) It is obtained commercially from the semi-solid portion of the coal tar distillate, which comes over at from 644° to 752° F. (340° to 400° C.) It is important to note that when distilled *at the lower temperature*, the anthracene is mixed with naphthalene, but that when distilled *at the higher temperature* it is mixed with chrysene and pyrene, these latter being the final products of the distillation of coal tar. Inasmuch, however, as anthracene is a valuable commercial product used in the preparation of artificial alizarine, and that alizarine cannot be produced either from naphthalene or from chrysene, the exact relation of anthracene to these bodies becomes important.

(2.) By passing benzene, mixed either with (α) ethylene, (β) with cinnamene, or (γ) with naphthalene vapor, through a red hot tube:—

(α.)	$2C_6H_6$	+	C_2H_4	=	$3H_2$	+	$C_{14}H_{10}$	
	Benzene	+	Ethylene	=	Hydrogen	+	Anthracene	
(β.)	C_6H_6	+	C_8H_8	=	$2H_2$	+	$C_{14}H_{10}$.	
	Benzene	+	Cinnamene	=	Hydrogen	+	Anthracene.	
(γ.)	$3C_6H_6$	+	$C_{10}H_8$	=	$3H_2$	+	$2C_{14}H_{10}$.	
	Benzene	+	Naphthalene	=	Hydrogen	+	Anthracene.	

(3.) By the action of heat on a mixture of (α.) ethylene and diphenyl or (β.) of ethylene and chrysene:—

(α.)	C_2H_4	+	$C_{12}H_{10}$	=	$2H_2$	+	$C_{14}H_{10}$.	
	Ethylene	+	Diphenyl	=	Hydrogen	+	Anthracene.	
(β.)	C_2H_4	+	$C_{18}H_{12}$	=	C_6H_6	+	$C_{14}H_{10}$.	
	Ethylene	+	Chrysene	=	Benzene	+	Anthracene.	

(4.) By the action of heat on toluene, xylene, or cumene.

(5.) By the action of heat on benzylic chloride:—

$4C_7H_7Cl$	=	$C_{14}H_{10}$	+	$C_{14}H_{14}$	+	4HCl.	
Benzylic chloride	=	Anthracene	+	Benzyltoluene	+	Hydrochloric acid.	

(6.) By the action of heat on a mixture of alizarine and zinc dust. Probably some of the alizarine is decomposed and hydrogen set free. The action may be formulated thus:—

$C_{14}H_8O_4$	+	H_2	+	4Zn	=	$C_{14}H_{10}$	+	4ZnO.
Alizarine	+	Hydrogen	+	Zinc	=	Anthracene	+	Zincic oxide.

Properties.—(α.) *Physical.* A colorless solid, crystallizing in four or six-sided plates. Specific gravity, 1·147. It sublimes at 212° F. (100° C.); melts at 415·4° F. (213° C.), and boils at 680° F. (360° C.). [Naphthalene melts at 176° F. (80° C.), and boils at 413·6° (212° C.)] Anthracene is insoluble in water, almost insoluble in cold alcohol (in which naphthalene is soluble), somewhat soluble in carbonic disulphide and in boiling alcohol; soluble in ether, in benzene, and in the volatile

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oils (such as turpentine). Sunlight in time effects its physical transformation into *paranthracene*, a body that melts at 471·2° F. (244° C.), but which may be reconverted by fusion into common anthracene.

(β.) *Chemical.*—With nascent hydrogen, it forms a dihydride, $C_{14}H_{10},H_2$. With the haloids it forms both substitution and additive products (as $C_{14}H_8Br_2.Br_4$).

Its reaction with oxidizing bodies is of great importance, inasmuch as by this means artificial alizarin, a body identical with the red coloring matter of madder, and a product of great commercial value, is prepared. The equations representing the reactions that occur in its preparation may be thus stated :—

(1.) (α.) Heated with nitric acid, or with potassic bichromate and sulphuric acid, *anthracene* forms *anthraquinone.* Thus :—

$2C_{14}H_{10}$	+	$3O_2$	=	$2[C_{14}H_8(O_2)'']$	+	$2H_2O$.
Anthracene	+	Oxygen	=	Anthra-quinone	+	Water.

In anthraquinone it will be noted that (O_2), like (Hg_2) in mercurous compounds, plays the part of a dyad radical.

[N.B. This body is called anthraquinone because it bears the same relationship to anthracene that quinone bears to benzene. Thus :—

C_6H_6	—	$C_6H_4(O_2)''$;	$C_{14}H_{10}$	—	$C_{14}H_8(O_2)''$.]
Benzene	—	Quinone ;	Anthracene	—	Anthraquinone.]

(β.) When anthraquinone is heated with bromine it forms dibrom-anthra-quinone. Thus :—

$C_{14}H_8O_2$	+	$2Br_2$	=	$C_{14}H_6Br_2O_2$	+	2HBr.
Anthra-quinone	+	Bromine	=	Dibrom-anthra-quinone	+	Hydrobromic acid.

(γ.) When dibrom-anthra-quinone is heated to 350° F. (176·1° C.) with potassic hydrate, it forms the potassic derivative of dioxy-anthra-quinone (or alizarin). Thus :—

$C_{14}H_6Br_2O_2$	+	4KHO	=	$C_{14}H_6O_2(KO)_2$	+	2KBr	+	$2H_2O$.
Dibrom-anthra-quinone	+	Potassic hydrate	=	Potassic alizarate	+	Potassic bromide	+	Water.

(δ.) When an acid is added to a solution of the fused mass containing potassic alizarate, crude alizarin, $C_{14}H_8O_4$ or $C_{14}H_6(OH)_2(O_2)''$, is thrown down as a yellow precipitate, which when carefully sublimed produces a red sublimate of fine alizarin.

Alizarin may also be prepared as follows :—

(2.) (α.) By the action of chlorine on anthracene, dichlor-anthracene is formed. Thus :—

$C_{14}H_{10}$	+	$2Cl_2$	=	$C_{14}H_8Cl_2$	+	2HCl.
Anthracene	+	Chlorine	=	Dichlor-anthracene	+	Hydrochloric acid.

(β.) When this dichlor-anthracene is heated with sulphuric acid it forms dichlor-anthracene-disulphonic acid $[C_{14}H_6Cl_2(HSO_3)_2]$. Thus:—

$C_{14}H_8Cl_2$	+	$2H_2SO_4$	=	$C_{14}H_6Cl_2(HSO_3)_2$	+	$2H_2O$.
Dichlor-anthracene	+	Sulphuric acid	=	Dichlor-anthracene disulphonic acid	+	Water.

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(γ.) By acting on this product with oxidizing agents, or by heating it with strong sulphuric acid, it forms anthraquinone-disulphonic acid $C_{14}H_6O_2(HSO_3)_2$. Thus:—

$C_{14}H_6Cl_2(HSO_3)_2$	+	O_2	=	$C_{14}H_6O_2(HSO_3)_2$	+	Cl_2.
Dichloranthracene disulphonic acid	+	Oxygen	=	Anthra-quinone-disulphonic acid	+	Chlorine.

(δ.) When this is heated with potassic hydrate it forms potassic alizarate, which is then treated with an acid in the manner already described.

$C_{14}H_6O_2(HSO_3)_2$	+	6KHO	=	$C_{14}H_6O_2(KO)_2$	+	$2K_2SO_3$	+	$4H_2O$.
Anthra-quinone-disulphonic acid	+	Potassic hydrate	=	Potassic alizarate	+	Potassic sulphite	+	Water.

Alizarin is soluble in alkaline solutions, and in solutions of the alkaline carbonates, forming deep purple liquids, from which alizarin may be precipitated by an acid.

Coal tar oil contains several bodies that are isomers of anthracene. For example, *phenanthrene* a solid, melting at 212° F. (100° C.), and boiling at 644° F. (340° C.); *tolane*, a solid, melting at 140° F. (60° C.); and a third body melting at 476·6° F. (247° C.).

NOTE.—We may here note, that, starting from benzene, we have a complete series of hydrocarbons, where the successive terms differ by C_4H_2. Thus:—

	Formula.	Fusing point.		Boiling point.	
		°F.	°C.	°F.	°C.
Benzene	C_6H_6	41·9	5·5	176·9	80·5
Naphthalene	$C_{10}H_8$	176·0	80·0	413·6	212·0
Anthracene	$C_{14}H_{10}$	415·4	213·0	680·0	360·0
Chrysene	$C_{18}H_{12}$	478·4	248·0		

The relationship of these bodies is remarkable. They all form *Quinones*, that is, bodies where H_2 is replaced by $(O_2)''$ *directly* (in all cases except that of benzene) as products of their oxidation (*see* page 528). These quinones are neutral bodies, and furnish hydro-quinones (the dioxy-derivatives of the several hydrocarbons), by the action of nascent hydrogen. Thus:—

C_6H_6	—	$C_6H_4(O_2)''$	—	$C_6H_4(OH)_2$.
Benzene	—	Quinone	—	Hydroquinone.

SERIES XI.—*Formula* C_nH_{2n-16} Series.

This includes only *stilbene* or *toluyene* ($C_{14}H_{12}$). This hydrocarbon is a crystalline solid, prepared by the action of heat on dibenzyl

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($C_{14}H_{14}=C_{14}H_{12}+H_2$). It melts at 212° F. (100° C.), and boils at 557·6° F. (292° C.). It forms both substitution and additive products. By the action of potassic hydrate on the dibromide $C_{14}H_{12}Br_2$, *tolane* ($C_{14}H_{10}$) is formed.

Series XII.—*Formula* C_nH_{2n-22} Series.

This includes—

		Fusing point.		
		°F.	°C.	
$C_{16}H_{10}$	Diacetenylbenzene Pyrene $C_{10}H_6(C_6H_4)$	287·6	142·0	Present in coal tar oil. (N.B.—These bodies contain 95 per cent. of carbon.)
$C_{18}H_{14}$	Diphenylbenzene $C_6H_4(C_6H_5)_2$	401·0	205·0	Obtained, with other products, by passing benzene through red-hot tubes. It yields an oxidation, first *phenylbenzoic* acid $C_6H_5C_6H_4(CO_2H)$, and finally *terephthalic* acid $C_6H_4(CO_2H)_2$.
$C_{19}H_{16}$	Triphenylbenzene $CH(C_6H_5)_3$	198·5	92·5	*Preparation.*—By the action of heat in closed tubes on a mixture of benzylene chloride, and mercuric phenyl.

Series XIII.—*Formula* C_nH_{2n-24} Series.

Chrysene ($C_{18}H_{12}$). This, the only known member of the series, is found together with pyrene ($C_{16}H_{10}$) as the final product of the distillation of coal tar. It crystallizes in fine yellow scales, which melt at from 473° to 478·4° F. (245° to 248° C.). It is insoluble in alcohol, and nearly insoluble in ether, but is soluble in boiling turpentine, from which it is deposited as the liquid cools. By oxidation it forms *chrysoquinone* ($C_{18}H_{10}O_2$).

Series XV.—*Formula* C_nH_{2n-32} Series.

This includes *tetraphenylethylene* ($C_2(C_6H_5)_4=C_{26}H_{20}$), a crystalline body which melts at 428° F. (220° C.), and is prepared by the action of heat on a mixture of finely divided silver and diphenylketone, this latter body being a product of the action of phosphorus pentachloride on benzophenone. Thus—

$$2[(C_6H_5)_2CCl_2] + 2Ag_2 = C_2(C_6H_5)_4 + 4AgCl.$$

Diphenylketone + Silver = Tetraphenylethylene + Argentic chloride.

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SUPPLEMENT TO CHAPTER ON THE HYDROCARBONS.

ADDENDUM TO THE PARAFFINS.

Petroleum—Paraffins.

The paraffins, it will be noted, vary greatly in their physical conditions. The higher terms are *solid*, and are employed in the manufacture of candles, etc. Following these are a series of *buttery* compounds, used for lubricating purposes. Then follow compounds which are *liquid* and are used for burning in lamps; and finally, certain liquids volatile below 100° F. (37·8° C.) (*petroleum spirit*), that are used as solvents in the arts.

In *American petroleum* and in the mineral oils of a like nature found in or near the coal formation, and formed by the gradual decomposition of vegetable matter beneath the earth's surface, we have an admixture of numerous hydrocarbons of this group of paraffins. In order to prepare the oil for illuminating purposes, it is necessary that all the hydrocarbons volatile at a temperature above 100° F. (37·8° C.), (that is, all the hydrocarbons containing less than six carbon atoms), should be distilled off, otherwise the oil would be dangerous. The distillate constitutes what is called "*Petroleum spirit*," and is used as a solvent for caoutchouc and resinous bodies, whilst the liquid remaining in the retort is safe for burning in lamps.

Paraffin oil, which is also a mixture of the paraffin hydrocarbons, is obtained by the destructive distillation of such bodies as boghead cannel, peat, etc. The most volatile portions are used for illuminating purposes, and the least volatile (mixed with fatty oils, such as rape, cotton, etc.) are employed for lubricating machinery.

Paraffin.

If petroleum (Rangoon tar or rock oil), or paraffin oil be subjected to an intense cold, the separation of a solid body, called *paraffin*, takes place. This substance exists ready formed in such minerals as ozokerit, mineral wax, etc. It is a compound of several hydrocarbons of the CH_4 group, and is largely used for candles, etc. The following is an outline of its preparation:—

The crude tar resulting from the destructive distillation of boghead cannel, etc., is distilled. The distillate is first shaken up with a sodic hydrate solution, in order to remove all acid bodies. It is afterwards treated with sulphuric acid, to remove all basic substances such as naphthalene, etc. The residue of these operations, after being well washed, is distilled, and the solid distillate collected.

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Any liquid oils present in the mass are now extracted, first by a centrifugal apparatus, then by pressure in the cold, and finally by pressure at or about 105° F. (40·5° C.), so as to remove all hydrocarbons melting below this temperature. The residue is again treated with sulphuric acid, whereby all hydrocarbons other than paraffins, are charred. The paraffin collects on the surface of the acid, and is then removed. After being washed, it is melted in oils of low boiling-point, the solution decolorised by filtration through animal charcoal, and finally the volatile oils removed by distillation from the pure paraffin.

Properties.—(α.) *Physical.* A white waxy solid, without taste or smell. Its fusing-point varies, according to its source, from 104° F. (40° C.) to 140° F. (60° C.), the latter being the temperature at which the paraffin obtained from ozokerit melts. It boils at about 698° F. (370° C.). A continuous heat under pressure converts it into liquid hydrocarbons (Thorpe and Young). It is insoluble in water, slightly soluble in alcohol, very soluble in ether and in the fixed and volatile oils.

(β.) *Chemical.*—Paraffin is remarkable, as its preparation given above would indicate, for its resistance to most chemical reagents (*parum affinis*). When, however, it is heated continuously for several days with sulphuric acid and potassic dichromate, cerotic acid is formed ($C_{27}H_{54}O_2$), and when similarly treated with nitric acid, a mixture results of solid and liquid fatty acids. When melted paraffin is acted on with chlorine, it is gradually attacked, and gives off hydrochloric acid.

ADDENDUM TO THE "TURPENES."

Oil of Turpentine and its Allies.—The Turpenes.

The name *turpentine* is given to an oleo-resinous juice exuding from certain varieties of pines. *Common English turpentine* is obtained from the Scotch fir, the Pinus Australis and Pinus Tœda; *Venice turpentine* from the larch; *French turpentine* from the Pinus maritima, etc.

"Turpentine" is a solution of rosin in spirits of turpentine. When distilled, the residue in the retort, amounting to from 75 to 90 per cent., constitutes *rosin*, and the distillate, varying in quantity from 10 to 25 per cent., constitutes *turps*, or *spirits of turpentine*. In the case of the Boston turpentine, the distillate constitutes "camphine."

Properties of spirits of turpentine.—(α.) *Physical.* A colorless, mobile, peculiar smelling liquid. Sp. Gr. 0·864. It boils at 320° F. (160° C.). It is not very soluble in water, but is very soluble in alcohol, carbonic disulphide, and in ether, and is itself a solvent for iodine, sulphur, phosphorus, resinous and fatty matters, caoutchouc, etc. It is a powerful refractor of light.

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(β.) *Chemical.* When *French spirits of turpentine* is neutralised with an alkaline carbonate and distilled, it yields "terebenthene" ($C_{10}H_{16}$), a liquid boiling at 321·8° F. (161° C.), and having a Sp. Gr. of 0·864. It turns the plane of polarisation *to the left.* *English spirits of turpentine* similarly treated, yields "austraterebenthene," a liquid having a similar gravity and boiling-point to terebenthene, but turning the plane of polarisation *to the right.*

(1.) Both bodies (*i.e.*, *terebenthene* or *austraterebenthene*) when heated to 482° F. (250° C.), form two *levo-rotatory* oils, which may be separated by distillation; *viz.*, *austrapyrolene*, boiling at 352·4° F. (178° C.), and *metaterebenthene* ($C_{20}H_{32}$), boiling at 680° F. (360° C.).

(2.) By the action of air, turpentine becomes oxidised and forms a product of a resinous nature.

(3.) Spirits of turpentine, though insoluble in water, forms three hydrates: *viz.*, (α) a crystalline hydrate, $C_{10}H_{16},3H_2O$, soluble in water, fusing at 217° F. (102·8° C.); (β) a second crystalline hydrate, $C_{10}H_{16},2H_2O$, subliming at 480° F. (248·9° C.) formed by the action of heat on the former hydrate; and (γ) a liquid hydrate called *terpinole*, $(C_{10}H_{16})_2,H_2O$, having an odor of hyacinths, and obtained by distilling either of the former hydrates with sulphuric acid.

(4.) *Chlorine* and *bromine* are so rapidly absorbed by turpentine, that inflammation frequently results, HBr and HCl being formed, and carbon set free. Distilled with water and chloride of lime, chloroform is formed. With *iodine*, combustion does not usually occur. The solution of iodine in turpentine is green, and, as the heat increases during the progress of the chemical action, hydrochloric acid is evolved.

(5.) By the action of gaseous boric fluoride, or when the spirits of turpentine is digested with a little oil of vitriol in the cold, it yields two liquids, both of which are without action on a polarised ray; *viz.*, *terebene* ($C_{10}H_{16}$), a liquid boiling at 320° F. (160° C.), having the odor of thyme, and *colophene* or *diterebene* ($C_{20}H_{32}$), a liquid boiling at 600° F. (315·5° C.), and having a Sp. Gr. of 0·940 (vapor density 4·76). This latter liquid appears colorless by directly transmitted light, and blue by obliquely transmitted light.

(6.) *Common nitric acid* forms, with turpentine, acid products. The action of the fuming acid upon it is sufficiently energetic to cause combustion.

The following volatile or essential oils have the same composition as common spirits of turpentine ($C_{10}H_{16}$), viz., oils of lemon, orange, bergamot, lime, citron, neroli (?), caraway, camomile, coriander, elemi, gomart, hop, juniper, laurel, parsley, savin, thyme, valerian, wintergreen, cloves, etc. The oils of copaiba and cubebs ($C_{20}H_{32}$) are also polymeric with spirits of turpentine.

All these bodies form resinoid substances by exposure to air.

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They also form crystalline hydrates and artificial camphors, by the action of hydrochloric acid.

It will be convenient here to consider a few bodies, the exact relationship of some of which it is not easy to define.

I. Essential or Volatile Oils.

These hydrocarbons are found for the most part in the vegetable kingdom and in all parts of the plant: sometimes in the *seed*, as in the mustard; sometimes in the *rind of the fruit*, as in the orange; sometimes *in the flower*, as in the rose; sometimes in the *leaves*, as in the myrtle. A few only are found in the bodies of animals, such as *e.g.*, the oil of ants.

Preparation of the Volatile Oils.—(α.) By *pressure*. *Examples*—Oils of lemon, bergamot, laurel, etc.

(β.) By *distillation* with water. This is the common method of extracting the majority of these oils.

(γ.) By *fermentation and distillation*. This is illustrated in the preparation of the oils of bitter almond and mustard, where, after the seed has been crushed and mixed with water, the action of some nitrogenized body on certain compounds in the seed, develops the oil which is afterwards extracted by distillation.

(δ.) By *destructive distillation*. *Examples*—The volatile oils from peat, wood, coal, bones, etc.

(ε.) By *solution in a fixed oil* destitute of odor (such as poppy oil). *Examples*—Oils of geranium, jessamine, violet, heliotrope, etc.

(ζ.) By *chemical action*. *Example*—Oil of spiræa, from salicine.

Properties.—(α.) *Physical*. At ordinary temperatures these oils are usually liquid. Oil of aniseed, however, is a solid. Their color is mostly yellow when first prepared, but they rapidly darken by exposure to air from the absorption of oxygen, becoming finally a resinoid mass. Their odor is powerful. Their boiling point is usually above 212° F. (100° C.). They produce on paper a greasy stain *which is transient*, and dissipated by heat. Their specific gravities vary, but they are usually lighter than water.

(β.) *Chemical*. They are all combustible bodies, slightly soluble in water, the solution forming the officinal medicated waters. They are freely soluble in spirit (forming essences), from which solutions they are precipitated by water. They are soluble in fatty oils. By the action of cold they separate into a solid crystalline compound (camphor or stearoptene) and a liquid oil (elœoptene). They are destroyed by the action of acids. They are insoluble in potash, and are not saponified by alkalies.

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Essential Oils.

Isomers and Polymers of Turpentine.

Oils of	Specific Gravity.		Boiling Pt.		Direction of Rotation.	Source.	Remarks.
	Liquid.	Vapor.	° F.	° C.			
Turpentine ..	0·864	4·812	320	160·0	left	Coniferous trees	
Bergamot	0·869		361	182·8	right		See Oil of lemon.
Borneène		4·60	320	160·0	left		
Birch	0·847	5·28	313	156·1			
Camomile			347	175·0		Anthemidis flores	Contains the hydrocarbon $C_{10}H_{16}$, and an oxidized body, $C_{10}H_{16}O_2$.
Caraway	0·938	5·17	343	172·8	right		Contains *carvene* ($C_{10}H_{16}$) and *carvol* ($C_{10}H_{14}O$).
Cloves	0·918		289	142·8			
Elemi	0·849		345	173·9	left		
Hop					right		
Juniper	0·86		320	160·0	left		
Lemon	0·851	4·87	343	172·8	right		Contains, in common with many others, *hesperidene* ($C_{10}H_{16}$), and certain oxidized hydrocarbons.
Orange	0·83	4·64	356	180·0	right		See Lemon.
Parsley			320	160·0			
Pepper	0·864	4·73	333	167·2			
Savine			320	160·0			
Tolu	0·837		320	160·0			
Thyme		4·76	329	165·0	none		
Capivi	0·878		500	260·0	left		} $C_{15}H_{24}$
Cubebs	0·929		490	254·5	left		
Attar of Roses..			592	311·1			Contains a solid hydrocarbon, C_6H_{16}, and an oxidized product to which the scent is due.
Bitter Almond..						Amygdala amara	
Dill						Fructus anethi	Contains *anethene* ($C_{10}H_{16}$), and an oil, $C_{10}H_{14}O$.
Aniseed						Pompenella anisum	Contains a solid hydrocarbon, $C_{10}H_{18}$.
Horseradish ..							*Composition*, C_4H_9CNS.
Neroli..							See Oil of lemons.
Cardamoms ..							Ditto. It also contains a camphor, $C_{10}H_{16}3H_2O$.
Cajeput							Contains *cajuputol* ($C_{10}H_{16}.H_2O$).
Cinnamon.. ..	1·050						
Fennel							
Peppermint ..							Contains *menthene* ($C_{10}H_{18}$).
Sassafras	1·094						
Mustard	1·015						

II. Camphors.

Camphors are oxidized hydrocarbons, and are closely related to the essential oils.

Common camphor ($C_{10}H_{16}O$) is obtained from the wood of the Laurus Camphora, or camphor laurel, by boiling it in water, and condensing the camphor as it passes over, on straw placed at the head of the still. It is afterwards purified by sublimation. An oil distils over during the action, called *liquid camphor* or *oil of camphor* $(C_{10}H_{16})_2O$, which by exposure to air oxidizes and deposits common camphor.

Properties.—(*a.*) *Physical.* A white crystalline (octahedra) solid, volatile at ordinary temperatures. It has a specific gravity of 0·996. It fuses at 347° F. (175° C.) and boils at 399° F. (203·9° C.). It rotates a ray of light to the right (+47·4). It is very slightly

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soluble in water (1 in 2,000 parts, or 40 grains per gallon), but is freely soluble in alcohol, in ether, and in strong acetic acid.

(β.) *Chemical.* Camphor burns with a smoky flame. When distilled it yields the colorless compound *camphoric oxide* ($C_{10}H_{14}O_3$). Distilled with P_2S_5 or with phosphoric anhydride, it forms *cymene* ($C_{10}H_{14}$), and when similarly treated with PCl_5, it forms *cymene* and *hydro-chloric acid.* With nitric acid it forms *camphoric acid* ($C_{10}H_{16}O_4$), a dextro-rotatory body. It is acted on by bromine, forming $C_{10}H_{16}Br_2O$; other compounds are also formed by it with bromine, such as *monobromcamphor* ($C_{10}H_{15}BrO$). Chlorine is without action upon it. Heated in sealed tubes with an alcoholic solution of caustic soda, it is resolved into *camphol* ($C_{10}H_{18}O$) and *camphic acid* ($C_{10}H_{16}O_2$).

Borneo camphor ($C_{10}H_{18}O$) is an exudation from the Dryabalanops camphora. It crystallizes in prisms. By distillation it yields a volatile oil called *borneène* ($C_{10}H_{16}$), which is often sold in the market as camphor oil, or liquid camphor.

By oxidation with nitric acid, Borneo camphor forms common camphor; whilst, by the action of metallic sodium on a solution of common camphor in toluene, it may be converted into Borneo camphor.

Common camphor rotates a ray of light to the right. The *camphor contained in the oil of feverfew* rotates it to the left. *The camphor in the essential oils* of the N. O. Labiatæ are optically inactive. The camphoric acids respectively formed from these camphors by the action upon them of nitric acid, have similar optical effects to the camphors themselves, but if the right and the left rotatory acids be mixed together in equal proportions, the acid formed is found to be without action on the polarized ray.

III. Resins.

Resins are bodies which exude from plants, dissolved in the essential oil peculiar to the plant. They are for the most part oxidized terebenes, and are produced in the plant by the oxidation of their essential oils.

Preparation.—(1.) By simple exudation. *Example*—Copal.

(2.) By distilling the oil from the resin in which it is dissolved. *Example*—Common rosin.

(3.) By destructive distillation. *Examples*—Guiacum, pitch.

Properties.—(α.) *Physical.*—The resins are solid transparent bodies, sometimes crystallizable. They have no well-marked odor. They are easily fused, but they are not volatile. They are decomposed when heated in closed vessels. They are insoluble in water, but are soluble in spirit. They are electrical insulators, and yield, by friction, negative electricity.

(β.) *Chemical.*—The resins are combustible, and burn with a white flame. Many of them are acid to litmus (as, *e.g.*, sandarach and

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guiacum), and yield a lather when acted on with an alkaline lye. This mixture, however, differs from a soap solution in not being precipitated on the addition of common salt.

The resins generally are compounds of more than one resin; their exact proximate constitution is not, in the majority of cases, well understood.

Varieties of Resins.

Resins.	Source.
Common rosin (*colophony*) { Brown .. White ..	The residue of American turpentine (pinus abies). (Galipot). The residue of Bordeaux turpentine (pinus maritima).
Amber	A fossil resin.
Arnicin ($C_{20}H_{30}O_4$) ..	The active principle of arnica root (arnica radix).
Cannabin	Indian hemp (cannabis indica).
Capsicum resin	Obtained from the fruit of the capsicum.
Castorin	Castor is the dried preputial follicles and secretions of the beaver.
Copal	An exuded resin from certain extinct trees (hymenæa verrucosa ?). It is found beneath the ground.
Dammar resin	
Dragon's blood ($C_{20}H_{20}O_4$)	An exudation from the fruit of a palm (calamus draco).
Ergotin	An active constituent of ergot.
Guiacum resin	From the wood of guiacum officinale.
Jalap resin	From the jalap tubercles. It is insoluble in turpentine.
Koussin ($C_{31}H_{38}O_{10}$) ..	From kousso.
Lac	An exudation on certain trees (as the *ficus indica*) produced by the puncture of an insect (coccus).
Mastich	From the stem of the mastic or lentisk tree (pistachia lentiscus).
Mezereon resin	From the dried bark of the Daphne mezereum.
Burgundy pitch	From the stem of the spruce fir (abies excelsa).
Podophyllum resin ..	From podophyllum root.
Pyrethrin	From pellitory root.
Rhubarb resin	From rhubarb.
Rottlerin	From kamala.
Sandarach	From the juniperus communis.

1. *Common rosin* (colophony) is the residue of the distillation of turpentine. The quantity obtained varies from 75 to 90 per cent. of the turpentine employed. It is a mixture of two acid bodies, *viz.*, a crystallizable acid called *abietic acid* ($C_{44}H_{64}O_5$), and an amorphous acid called *pinic acid* ($C_{20}H_{30}O_2$).

2. *Lac* is an exudation from certain trees, occasioned by the puncture of an insect. "*Stick lac*" is the crude state in which the resin is collected. "*Seed lac*" is the resinous residue left after boiling the crude lac with a solution of sodic carbonate, in order to extract from it a red-coloring matter (lac-dye) used by the dyer. "*Shellac*" is the fused "seed-lac." This resin is largely used for hats, sealing-wax, and varnishes. "*Indian ink*" consists of a mixture of shellac (100 grs.), borax (20 grs.), lampblack and water (4 ozs.). "*Lacquer*" is an alcoholic solution of shellac, sandarach, and Venice turpentine.

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3. *Amber* is a fossil resin found accompanying lignite. It is soluble in alcohol (1 part in 8), and in ether (1 in 10). It is more soluble in these liquids after it has been fused than before. When acted on with nitric acid or digested with alkalies, it yields succinic acid.

4. *Copal* differs from other resins by its comparatively slight solubility in alcohol and in essential oils. When melted, however, it mixes with oils, and is thus made into varnish.

5. *Guiacum resin* is the exudation from the wood of the guiacum officinale. It is soluble in alcohol. Oxidizing agents, under the influence of certain organic substances, produce a blue, green, and brown color with the alcoholic solution.

Uses of Resins.—For varnishes. For stiffening purposes; for yellow soap, and for sealing-wax.

In the manufacture of varnishes, the powdered resin (copal, mastic, sandarach, lac, elemi and anime being those most frequently used) is mixed with some powdered glass, so as to prevent its becoming lumpy. The solvents principally employed are turpentine, methylated alcohol and wood spirit; in the case of copal, mastic and sandarach, certain liquids such as acetone, a little turpentine or some fixed oil, (such as linseed or poppy) are commonly added to prevent the varnish cracking when dry (oil varnishes). Spirit varnishes dry rapidly; oil varnishes dry slowly, but are more durable.

IV. Gum Resins.

Definition.—Mixtures of a resin or of an oleo-resin and gum.

Gum resins form an emulsion when rubbed up with water, *i.e.*, the particles of resin are held in suspension by the solution of gum. The gum resins are soluble in dilute alcohol and in weak alkalies. They form a numerous class, amongst which may be mentioned ammoniacum, assafœtida, aloes, euphorbium, galbanum, gamboge, myrrh, olibanum or Arabian frankincense, and scammony.

V. Oleo-Resins.

Definition.—A mixture of a resin and a volatile oil.

This class includes copaiva, the turpentines, common frankincense, (Pinus Tœda), Canada balsam (the turpentine from the Balm of Gilead fir), sumbul root, etc.

VI. Balsams.

Definition.—A resin, or an oleo-resin, containing benzoic or cinnamic acid. (*Memo.* Balsam of Copaiba and Canada balsam are not true balsams, as they neither contain cinnamic nor benzoic acid).

This class includes benzoin (styrax benzoin), balsam of Peru (myroxylon Pereira), balsam of tolu (myroxylon toluifera), storax (liquidambar orientale), etc.

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India Rubber—Caoutchouc.

Natural History.—A milky juice, solidifying on exposure to air. It is obtained from many tropical plants, such as the Ficus elastica, etc.

Constitution.—A mixture of several isomers and polymers of turpentine oil.

Preparation.—The juice, which is perfectly white and liquid when first obtained, flows from incisions made in the tree, and is then dried on clay moulds.

Properties of the solid caoutchouc.—An elastic solid. Specific gravity 0·93. It melts at 250° F. (120·9° C.) When heated slightly beyond its melting-point, it forms a liquid which does not solidify on cooling. At a higher temperature it is decomposed into two liquids, viz., *isoprene* (C_5H_8), boiling at 98·6° F. (37° C.), and *caoutchine*, boiling at 339·8° F. (171° C.), and in both of which liquids caoutchouc is soluble. It is insoluble in alcohol or in water, but is softened by boiling water. It is soluble in ether, in naphtha, and in the volatile oils, and remains unchanged as the solvent evaporates. Neither alkalies, dilute acids, nor indeed chemical reagents generally, have any action upon it. It combines with about 2 to 3 per cent. of sulphur when melted in contact with it, forming "Vulcanized India Rubber," which is a more elastic body than rubber, but is insoluble in naphtha or in turpentine, and is incapable like rubber, of cohering to other surfaces with which it may be brought into contact.

Uses :—

1. For general cleansing purposes.
2. For waterproofing.
3. For *vulcanized India rubber.* Most specimens of vulcanized rubber contain more than 2 per cent. of sulphur. Under such circumstances the rubber after a short time becomes inelastic and brittle, owing to the oxidation of the free sulphur.
4. For *ebonite* (vulcanite). This is prepared by mixing caoutchouc with about half its weight of sulphur, and afterwards hardening the mixture by heat and pressure. It takes a high polish.
5. *Marine glue* is a solution of caoutchouc mixed with a little shellac, in coal tar naphtha.

Gutta Percha.

Natural History.—A milky juice exuding from the Isonandra percha, and solidifying by exposure to air.

Composition—Similar to that of caoutchouc.

Properties.—An inelastic solid; specific gravity 0·98. It is insoluble in water, alcohol, acids or alkalies, but is soluble in ether, volatile oils, chloroform, carbonic disulphide, naphtha, etc. It softens at 212° F. (100° C.) and decomposes at 400° F. (204·4° C.) It may be vulcanized like caoutchouc.

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CHAPTER XXIII.

THE ALCOHOLS.

Relation of Alcohols to other Bodies—Series of Alcohols—General preparation and properties of the members of the various Series—Mercaptans.

SUPPLEMENTARY CHAPTER: Sugar — Glucosides — Starches — Gums — Reaction of various Alcohols and allied Bodies.

The alcohols are saturated derivatives of the hydrocarbons, one or more atoms of the hydrogen of the hydrocarbon being replaced by a semi-molecule of hydroxyl (OH); in other words, the alcohols are compounds of hydroxyl and alcohol radicals.

(*a.*) If 1 hydrogen atom only of the hydrocarbon be replaced by 1 of the group (OH), a *monohydric alcohol* is formed. Thus $C_3H_7(OH)$, a derivative of C_3H_8, constitutes monohydric propylic alcohol.

(β.) If 2 or more hydrogen atoms be replaced by 2 or more of the group (OH), a *dihydric* (or trihydric, etc.) *alcohol* is formed. Thus $C_3H_5(OH)_3$ constitutes the trihydric alcohol glycerine.

The exact relationships of the alcohols must be noted.

Relation of the alcohols to the haloid ethers.—If the group or groups of (OH) in the alcohol, be replaced (partly or wholly) by chlorine, (as *e.g.*, by the action upon the alcohol either of a haloid acid, or of a compound of phosphorus with a haloid), a *haloid ether* is formed. Thus *propylic alcohol*, $C_3H_7(OH)$, forms *propane chloride*, $C_3H_7(Cl)$.

If this haloid ether be treated with potassic or sodic hydrate, the alcohol will be reformed; thus:—

$C_3H_7(Cl)$	+	KOH	=	$C_3H_7(OH)$	+	KCl.
Propane chloride	+	Potassic hydrate	=	Propylic alcohol	+	Potassic chloride.

Relation of the alcohols to the oxy-ethers.—If the group or groups of (OH) in the alcohol be replaced by potassoxyl (OK) or methyloxyl (OCH_3), etc., an *oxygen ether* is formed. Thus—

Ethylic alcohol ($C_2H_5(OH)$ forms $C_2H_5(OK)$, *potassic ethylate:*

,, ,, $C_2H_5(OCH_3)$, *methylic ethylate*, etc.

Relation of the alcohols to the compound ethers (ethereal salts).—If the hydrogen of the hydroxyl (OH) in the alcohol, be replaced by an acid radical, an *ethereal salt* is formed. Thus—

Methylic alcohol, $CH_3(OH)$, forms $CH_3(OC_2H_3O)$, *methylic acetate.*

Constitution.—An alcohol may be regarded as formed on the water type, where one atom of hydrogen is replaced by a compound radical. Thus—

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O = \underset{\textit{Ethylic alcohol;}}{C_2H_5(OH)} \qquad \left.\begin{matrix}C_3H_7\\H\end{matrix}\right\}O = \underset{\textit{Propylic alcohol.}}{C_3H_7(OH)}$$

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The alcohols may be arranged in the following groups :—

Series.	Formula.	Examples.
A.—Monohydric Alcohols—		
I. Ethylic series	$C_nH_{2n+1}(OH)$	Methylic alcohol $CH_3(OH)$.
II. Vinylic series	$C_nH_{2n-1}(OH)$	Vinylic alcohol $C_2H_3(OH)$.
III.	$C_nH_{2n-3}(OH)$	Propargylic alcohol $C_3H_3(OH)$.
IV.	$C_nH_{2n-5}(OH)$	
V. Benzylic series.. ..	$C_nH_{2n-7}(OH)$	Phenol $C_6H_5(OH)$.
VI. Cinnamic series ..	$C_nH_{2n-9}(OH)$	Cinnamic alcohol $C_9H_9(OH)$.
VII.	$C_nH_{2n-13}(OH)$	
B.—Dihydric Alcohols—		
I. Glycols	$C_nH_{2n}(OH)_2$	Glycol $C_2H_4(OH)_2$.
II. Orcins	$C_nH_{2n-8}(OH)_2$	Orcin $C_6H_3(CH_3)(OH)_2$.
C.—Trihydric Alcohols—		
I. Glyceric series	$C_nH_{2n-1}(OH)_3$	Glycerin $C_3H_5(OH)_3$.
II. Pyrogallic series ..	$C_nH_{2n-9}(OH)_3$	Pyrogallol $C_6H_3(OH)_3$.
D.—Tetrahydric Alcohols—	$C_nH_{2n-2}(OH)_4$	Erythrite $C_4H_6(OH)_4$.
E.—Hexhydric Alcohols—	$C_nH_{2n-4}(OH)_6$	Mannite $C_6H_8(OH)_6$.

A.—MONOHYDRIC ALCOHOLS.

Ethylic Series.

Series I.—*Formula* $C_nH_{2n+1}(OH)$.

This includes—

Alcohols.	Formula.	Specific Gr. at ° C.	Boiling Pt. ° F.	Boiling Pt. ° C.	Vapor Density.	Source.
1. Methylic (wood naphtha)	$CH_3(OH)$	0·798 at 20	151·0	66·1	1·12	Destructive distillation of wood.
2. Ethylic (spirits of wine)	$C_2H_5(OH)$	0·7938 at 15	173·0	78·3	1·61	Fermentation of sugar.
3. Propylic	$C_3H_7(OH)$	0·8205 at 0	206·0	96·6	2·02	Ditto of grape husks.
4. Butylic	$C_4H_9(OH)$	0·8032 at 18	233·0	111·7	2·59	Ditto of beet root.
5. Amylic (fusel oil ; pentylic)	$C_5H_{11}(OH)$	0·8111	269·8	132·1	3·15	Ditto of potatoes.
6. Hexylic (caproic)..	$C_6H_{13}(OH)$	0·819 at 23	309·0	153·9	3·53	Ditto of grape husks.
7. Œnanthic(heptylic)	$C_7H_{15}(OH)$		343·0	172·8		Distillation of castor oil with KHO.
8. Caprylic (octylic)..	$C_8H_{17}(OH)$	0·8717 at 16	356·0	180·0	4·50	Fermentation of grape husks.
9. Nonylic	$C_9H_{19}(OH)$		392·0	200·0		
10. Rutic (decatylic) ..	$C_{10}H_{21}(OH)$		414·0	212·2		Oil of rue.
11. Lauric	$C_{12}H_{25}(OH)$					Whale oil.
12. Cetylic (ethal) ..	$C_{16}H_{33}(OH)$					Spermaceti ; fuses at 122° F.
13. Cerylic(cerotene)..	$C_{27}H_{55}(OH)$					Chinese wax ; fuses at 174° F.
14. Melissic (melissine)	$C_{30}H_{61}(OH)$					Beeswax ; fuses at 185° F.

Isomeric forms.—All these alcohols (excepting the two first terms) have numerous isomeric modifications. They are distinguished partly by their different physical properties, such as by their different boiling-points, but more especially by their behaviour on oxidation. To Kolbe we are indebted for a systematic arrangement of these iso-

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merides. To methylic alcohol ($CH_3.OH$) he has given the name *carbinol*, whilst all the succeeding alcohols he terms *carbinols*, regarding them as derivatives of the first term (methylic alcohol), and formed by the replacement of hydrogen by monad radicals of the form C_nH_{2n+1}:

(α.) If, judging by its preparation and by its mode of formation, the alcohol be formed by the replacement of 1 unit of hydrogen of the carbinol by the compound group (C_nH_{2n+1}), the alcohol is then called a *primary alcohol*. Thus, ($CH_3.OH$) being carbinol—

$CH_2(CH_3)OH$ is the primary alcohol *methyl carbinol* (ethylic alcohol).
$CH_2(C_2H_5)OH$,, ,, *ethyl carbinol* (propylic alcohol).

(β.) If two units of hydrogen of the carbinol be replaced by 2 of the group (C_nH_{2n+1}), the alcohol is then called a *secondary alcohol*. Thus—

$CH(CH_3)(CH_3)OH$ is the secondary alcohol *dimethyl carbinol* (propylic alcohol).
$CH(C_2H_5)(CH_3)OH$,, ,, *ethylmethyl carbinol* (butylic alcohol).

(γ.) If three units of hydrogen of the carbinol be replaced by three of the group (C_nH_{2n+1}), the alcohol is then called a *tertiary alcohol*. Thus—

$C(CH_3)(CH_3)(CH_3)OH$ is the tertiary alcohol *trimethyl carbinol* (butylic alcohol).
$C(C_2H_5)(CH_3)(CH_3)OH$,, ,, *ethyldimethyl carbinol* (amylic alcohol).

It will therefore be understood that an alcohol is regarded as primary, secondary, or tertiary, according as the carbon atom in combination with the hydroxyl group, is also directly combined with 1, 2, or 3 other carbon atoms. It will further be evident why no isomeric modifications of methylic or ethylic alcohol are possible.

The following list includes the principal *secondary alcohols*:—

	Formula.	Boiling point.	
		°F.	°C.
Dimethyl carbinol	$CH(CH_3)_2OH$	185	85·0
Ethyl methyl carbinol	$CH(CH_3)(C_2H_5)OH$	207	97·2
Methyl-isopropyl carbinol	$CH.CH(CH_3)_3OH$	226	107·8
Methyl propyl carbinol	$CH(CH_3)(C_3H_7)OH$	248	120·0
Methyl butyl carbinol	$CH(CH_3)(C_4H_9)OH$	277	136·1
Methyl pentyl carbinol	$CH(CH_3)(C_5H_{11})OH$	320	160·0
Methyl hexyl carbinol	$CH(CH_3)(C_6H_{13})OH$	358	181·1
Methyl nonyl carbinol	$CH(CH_3)(C_9H_{19})OH$	445	225·5

The following *tertiary alcohols* are known:—

	Formula.	Boiling point.	
		°F.	°C.
Trimethyl carbinol..	$C(CH_3)_3OH$	179	
Dimethyl ethyl carbinol	$C(CH_3)_2(C_2H_5)OH$	212	
Dimethyl isopropyl carbinol	$C(CH_3)_2(CH_3)_2CH.OH$	234	
Dimethyl propyl carbinol	$C(CH_3)_2(C_3H_7)OH$	239	
Methyl diethyl carbinol..	$C(CH_3)(C_2H_5)_2OH$	248	
Triethyl carbinol	$C(C_2H_5)_3OH$	284	
Diethyl propyl carbinol..	$C(C_2H_5)_2(C_3H_7)OH$		

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It will be convenient here to note the different effects of oxidizing agents on these three classes of alcohols:—

(α.) *Primary alcohols.*—These yield, by oxidation, three products; *viz.*, (1) an *aldehyde;* (2) a *monobasic acid;* and (3) an *ethereal salt*, the relative quantities of each of these products being dependent on many causes, such as the temperature, the alcohol, the oxidising agent, and the quantity of water present. Thus:—

(1.) $CH_3CH_2(OH) + O = CH_3COH + H_2O.$
Ethylic alcohol + Oxygen = Acetic aldehyde + Water.

(2.) $CH_3COH + O = CH_3COOH.$
Acetic aldehyde + Oxygen = Acetic acid.

(3.) $CH_3COOH + C_2H_5(OH) = CH_3COO(C_2H_5) + H_2O.$
Acetic acid + Ethylic alcohol = Ethylic acetate + Water.

Thus a primary alcohol yields on oxidation, an aldehyde, an acid containing the same number of carbon atoms as the alcohol oxidised, and an ethereal salt.

(β.) *Secondary alcohols.*—These yield *no aldehyde* on oxidation, but (1) a *ketone*, which, by the prolonged action of the oxidising agent, becomes (2) *an acid*, but *which acid contains a less number of carbon atoms than the alcohol oxidised.*

(γ.) *Tertiary alcohols.*—These yield *no ketone*, and *no aldehyde* on oxidation, but *one or more acids of the acetic series.* Possibly a ketone may be formed, but it has never yet been discovered.

Preparation (General Methods) of the Normal Primary Alcohols.

(1.) *From the paraffins* (C_nH_{2n+2}).—This is illustrated in the preparation of methylic alcohol from methane (CH_4), as follows:—

(α.) A monochlorinated derivative of the paraffin is first formed, by the action of chlorine on the paraffin. Thus:—

$CH_4 + Cl_2 = HCl + CH_3Cl.$
Methane + Chlorine = Hydrochloric acid + Methyl chloride.

(β.) By the action of argentic acetate on this chlorinated derivative, an ethereal salt is formed. Thus, *e.g.*:—

$CH_3Cl + AgC_2H_3O_2 = AgCl + CH_3(C_2H_3O_2).$
Methyl chloride + Argentic acetate = Argentic chloride + Methylic acetate.

(γ.) By the action of potassic hydrate on this ethereal salt, potassic acetate and methylic alcohol are formed.

$CH_3(C_2H_3O_2) + KHO = CH_3(OH) + KC_2H_3O_2.$
Methylic acetate + Potassic hydrate = Methylic alcohol + Potassic acetate.

[Conversely it may be noted that the alcohol may be converted into its corresponding paraffin by first forming from it a chlorine derivative, and then acting on the chlorine derivative with nascent hydrogen (*see* page 530).]

(2.) *From the olefines* (C_nH_{2n}).—This may be effected by two

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methods, which may be illustrated in the formation of ethylic alcohol from ethylene (C_2H_4) :—

(A.) (*First process.*) (α.) The olefine is first acted on with sulphuric acid, whereby an acid ether of sulphuric acid is formed. Thus :—

C_2H_4	+	H_2SO_4	=	$C_2H_5.HSO_4$.
Ethylene	+	Sulphuric acid	=	(Sulpho-vinic acid) or hydric ethylic sulphate.

(β.) This ethereal salt is now distilled with water, when the alcohol and sulphuric acid are formed. Thus :—

$C_2H_5.HSO_4$	+	H_2O	=	$C_2H_5(HO)$	+	H_2SO_4.
Sulpho-vinic acid	+	Water	=	Ethylic alcohol	+	Sulphuric acid.

(B.) (*Second process.*) (α.) By the action of hypochlorous acid on the olefine, a monochlorinated monohydric alcohol is formed. Thus :—

C_2H_4	+	HClO	=	$C_2H_4Cl(OH)$.
Ethylene	+	Hypochlorous acid	=	Chlorinated ethylic alcohol.

(β.) When this is acted on with nascent hydrogen, the alcohol and hydrochloric acid are formed,

$C_2H_4Cl(OH)$	+	H_2	$=C_2H_5(OH)+$	HCl.
Chlorinated ethylic alcohol	+	Hydrogen	= Ethylic alcohol	+ Hydrochloric acid.

[Conversely, by the abstraction of the elements of water, the olefine may be prepared from the alcohol. Thus :—

$C_2H_5(OH)$	—	H_2O	=	C_2H_4.]
Ethylic alcohol	—	Water	=	Acetylene.]

(3.) *From the normal primary* (α) *aldehydes*, or *from the* (β) *anhydrides of the acetic series.*—By the action of nascent hydrogen in each case :—

(α.) $H(COH) + H_2 = CH_3(OH)$; $CH_3(COH) + H_2 = C_2H_5(OH)$.

Formic aldehyde + Hydrogen = Methylic alcohol ; Acetic aldehyde + Hydrogen = Ethylic alcohol.

[By the action of nascent hydrogen on the isoprimary aldehydes of the acetic series, isoprimary alcohols are formed.]

(β.) $\left.\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\right\}O + 4H_2 = 2[C_2H_5(OH)] + OH_2$.

Acetic anhydride + Hydrogen = Ethylic alcohol + Water.

(4.) One alcohol may be prepared *from the alcohol immediately preceding it in the series.*—Thus formic aldehyde yields methylic alcohol, and methylic alcohol may be made to yield ethylic alcohol. Thus :—

(α.) *Iodomethane* (CH_3I) is first formed by the action of hydriodic acid on methylic alcohol.

(β.) *Cyanomethane* ($CH_3(CN)$) is then formed by the action of potassic cyanide on iodomethane.

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(γ.) *Sodic acetate* ($NaC_2H_3O_2$) is formed by digesting cyanomethane with sodic hydrate.

(δ.) *Acetic aldehyde* (CH_3COH) is formed by distilling sodic acetate with potassic formate.

(ε.) *Ethylic alcohol* ($C_2H_5(OH)$) is formed by the action of nascent hydrogen on acetic aldehyde.

Similarly normal primary propylic alcohol may be prepared from ethylic alcohol, etc.

Normal secondary alcohols are prepared (α) by the action of nascent hydrogen on the normal primary ketones, and (β) from the normal primary paraffins.

Tertiary alcohols may be prepared by the action of water on the product formed by the action of the zinc organo-metallic compounds on the acid chlorides of the form $C_nH_{2n+1}COCl$.

General Properties.—(α.) *Physical.* — All the alcohols of the ethylic series are colorless, and possess a more or less powerful odor. The first nine are colorless liquids. The first two (methylic and ethylic alcohol) are mobile liquids, and are soluble in water in all proportions, but the third (propylic alcohol) has not unlimited solubility. From this point the liquids get thicker, their boiling points higher, and their solubility in water less. Thus butylic alcohol is not very soluble, amylic alcohol is very sparingly soluble, and hexylic alcohol is insoluble in water. Caprylic alcohol leaves a greasy stain when dropped on paper. From nonylic alcohol downwards, the members of the series are solid.

One molecule in each case yields two molecules of vapor.

(β.) *Chemical.* With *phosphorus pentasulphide*, the ethylic series form mercaptans or sulphydrates ($5(C_2H_5(OH))+P_2S_5=5(C_2H_5(SH))$ (*ethylic sulphydrate*) $+ P_2O_5$); with *oxyacids* they form ethereal salts ($C_2H_5(OH) + HNO_3 = (C_2H_5)NO_3$ (*ethylic nitrate*) $+ H_2O$); with *haloid acids* or with *compounds of phosphorus and the haloids*, they form monohaloid derivatives of the corresponding paraffins ($CH_3(OH) + HI = CH_3I$ (*iodomethane*) $+ H_2O$); with the *alkaline metals*, hydrogen is evolved, and a metallic derivative formed ($2(C_2H_5(OH)) + Na_2 = 2(C_2H_5(ONa))+H_2$), which metallic derivative is decomposed by water, with the formation of a metallic hydrate and the alcohol ($C_2H_5(ONa) + H_2O = C_2H_5(OH) + NaHO$). Their reactions *with oxidizing agents* have been described (p. 560), whilst *with dehydrating agents* the corresponding olefine is formed by the abstraction of water ($C_2H_5(OH) - H_2O = C_2H_4 + H_2O$).

(1.) Methylic Alcohol. (CH_3OH) or Me(OH). [*Molecular weight* 32. *Molecular volume* $\square$. *Specific gravity*, 0·798. *Boils at* 151·7° F. (66·5° C.) 100 c.i. *of the vapor weigh* 24·684 *grs., and* 1 *litre* 1·433 *grms.*]

Synonyms.—Carbinol; Wood or Pyroxylic spirit; Hydroxymethane; Pyroligneous ether.

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Preparation.—1. From the paraffin methane (General Methods, 1).

2. From formic aldehyde (General Methods, 3 (*a*).

3. By the action of potassic hydrate on the oil of the Gaultheria procumbens (wintergreen; methylic salicylate).

[This oil was the first vegetable product prepared artificially. Thus:—By the action of potassic hydrate on salicin, salicylic acid is formed, and this, when distilled with wood spirit and sulphuric acid yields the artificial oil.]

$$C_6H_4(OH).CO_2.CH_3 + KHO = C_6H_4(OH).CO_2K + CH_3(OH).$$

Methylic salicylate + Potassic hydrate = Potassic salicylate + Methylic alcohol.

4. By the action of heat on the nitrite of methylamine:—

(*a.*) Methylamine is formed by the action of nascent hydrogen on hydrocyanic acid; thus—

$$HCN + 2H_2 = CH_3.H_2N.$$

Hydrocyanic acid + Hydrogen = Methylamine.

(*β*). By boiling the solution of nitrite of methylamine, nitrogen, water, and methylic alcohol are formed; thus—

$$CH_3.H_3N(NO_2) = N_2 + H_2O + CH_3(OH).$$

Nitrite of methylamine = Nitrogen + Water + Methylic alcohol.

5. *Commercial process.* It is prepared from the watery liquid, or *crude wood vinegar* as it is called, produced by the destructive distillation of wood, and which contains 1 part of naphtha and 20 parts of acetic acid.

This watery liquid is first of all distilled, the portion that distils over at a temperature below 212° F. (100° C.), being collected separately. This contains methylic alcohol, acetone, acetate of methyl, and certain oily substances to which its odor is largely due. To this distillate slaked lime is added, and the clear liquor (that is, the liquid drawn from the centre, by which means the lime which sinks and the oil that floats are avoided) is several times redistilled. This distillate is now saturated with calcic chloride, whereby a crystalline compound ($CaCl_2,4CH_4O$), containing four molecules of methylic alcohol and one molecule of calcic chloride, is formed. This solid residue is now heated below 212° F. (100° C.), (beyond which temperature it would be decomposed), to drive off any acetone or methylic acetate present. Water is now added to the dried residue to decompose it, and the alcohol distilled off. Finally the methylic alcohol is purified by rectification, and rendered anhydrous by distillation after digestion with powdered quicklime.

The purest methylic alcohol is prepared by the action of water on methylic oxalate.

Properties.—(*a.*) *Physical.* When *pure*, methylic alcohol is a thin colorless liquid, having a taste and odor very like ethylic alcohol. The *crude alcohol* has an offensive odor and a burning taste. Specific

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gravity 0·798 at 20° C. Boiling point 151·7° F. (66·5° C.). It mixes with water (condensation resulting) in all proportions, and it is (like ethylic alcohol) a solvent of resins, volatile oils, etc.

(β.) *Chemical.—It unites with certain salts* in the capacity of water of crystallization (*e.g.* $CaCl_2.2CH_3.OH$). It unites *with the alkaline metals*, forming methylates, hydrogen being evolved ($2CH_3.OH + K_2 = 2CH_3.OK + H_2$); it also dissolves caustic soda, potash, baryta, etc. ($BaO,2CH_4O$). *Distilled with chloride of lime and water* it forms chloroform (*see* Chloroform); by *oxidation*, as by exposure to air on platinum black, it yields formic acid ($CH_3(HO) + O_2 = H_2O + CH_2O_2$).

It burns in lamps yielding a pale-colored flame, which deposits no soot.

Uses.—In the arts it is employed as a solvent of resins for varnishes, and for burning in lamps as a *heating* power only. Also for mixing with pure alcohol to form *methylated spirit* (= ethylic alcohol 90 parts—methylic alcohol 10 parts. Specific gravity 0·83).

(2.) Ethylic Alcohol ($C_2H_5(OH)$ or Et (OH). [*Molecular weight* 46. *Molecular volume* $\boxed{\ |\ |\ }$. *Specific gravity* 0·7938 *at* 15° C. *Boiling point* 173° F. (78·4° C.).]

Synonyms.—Alcohol; Vinic alcohol; Spirits of wine; Methyl carbinol, $CH_3(CH_2OH)$; *Hydroxyl ethene.*

Preparation.—(1.) From the olefine ethylene, C_2H_4 (*see* General Methods 2).

[Note. Ethylene may be prepared by the direct union of carbon and hydrogen.]

(2.) By the fermentation of grape sugar.

Properties.—A colorless liquid having an agreeable taste and odor. It burns with a non-luminous smokeless flame, requiring three times its own volume of oxygen for complete combustion. When imperfectly burnt, an acrid volatile compound is formed. Anhydrous alcohol boils at 173° F. (78·3° C.) at standard pressure. By dilution the boiling point becomes gradually higher.

It has never been frozen.

Action of water on alcohol.—Alcohol is very hygroscopic, and mixes with water in all proportions, heat and contraction of volume resulting from their admixture.

To determine the amount of alcohol present in any mixture, a given quantity must be distilled until all the alcohol has passed over. The distillate is then to be weighed, and its specific gravity taken, the percentage of alcohol being determined by table (Table VII.).

Proof spirit (that is the weakest spirit that will fire gunpowder when moistened with it and ignited), has a gravity of 0·92 and contains in every 100 parts by weight—

Water	...	...	...	50·76.
Alcohol	...	...	...	49·24.

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A weaker spirit does not fire gunpowder, and is termed "*under proof*," a stronger spirit being spoken of as "*over proof*."

By distillation, a weak spirit may be made to yield a 90 per cent. alcohol (that is, a spirit containing 90 per cent. of alcohol), but distillation will not effect the separation of the last 10 per cent. of water. A further separation of 5 per cent. of water (that is, the formation of a 95 per cent. alcohol) may be effected by enclosing the alcohol in a bladder, through which the water exudes more rapidly than the alcohol. An alcohol of 89 per cent. may be obtained by dissolving dry potassic carbonate in the alcohol to saturation. The solution separates into two layers, the upper consisting of spirit of 89 per cent., and the lower of water, containing potassic carbonate in solution. Absolute alcohol (100 per cent.) is prepared by digesting the alcohol with quick lime for three or four days, and distilling. It is very hygroscopic.

Commercial rectified spirit contains 13 or 14 per cent. of water. Sp. Gr. 0·835.
„ proof „ 49·5 „ „ Sp. Gr. 0·9198.

Alcohol dissolves numerous salts, but no salts are soluble in alcohol that are insoluble in water. It dissolves most deliquescent salts, and but few efflorescent salts. With some it forms definite crystalline compounds, called alcoholates, *i. e.*, salts containing alcohol in the place of water of crystallization, as, *e. g.*, $ZnCl_2,2C_2H_6O$, etc. These bodies are decomposed by water. It also dissolves the *alkaline metals*, hydrogen being evolved forming C_2H_5KO and C_2H_5NaO; also the elementary gases O, H, and N; also the gaseous hydrocarbons; also certain organic bodies, such as the alkaloids, resins, essential oils, etc.

When the vapor of alcohol is passed through a red-hot tube, it yields marsh gas, carbonic oxide and hydrogen ($C_2H_6O=CH_4+H_2+CO$), other bodies, such as C_2H_6, C_6H_6, etc., being also formed.

Action of chlorine.—By the action of chlorine on *absolute alcohol*, continued until hydrochloric acid ceases to be evolved, ethylic acetate and chloral hydrate (trichloraldehyde) are formed :—

$$2C_2H_5.OH + 4Cl_2 = CCl_3.CH(OH)_2 + C_2H_5Cl + 4HCl.$$

Ethylic alcohol + Chlorine = Chloral hydrate + Ethylic chloride + Hydrochloric acid.

By the action of chlorine on *dilute alcohol*, aldehyde but no chloral is formed.

By the action of chlorine on alcohol *in the presence of alkalies* (or by the action on the alcohol of chloride of lime), chloroform and carbonic anhydride are formed. Thus—

$$C_2H_5(OH) + 5Cl_2 + H_2O = CO_2 + 7HCl + CHCl_3.$$

Ethylic alcohol + Chlorine + Water = Carbonic anhydride + Hydrochloric acid + Chloroform.

Numerous intermediate products may also be formed.

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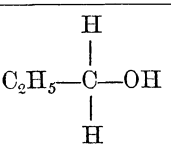
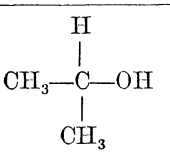
By *oxidation* alcohol (C_2H_6O) is converted into aldehyde (C_2H_4O), and finally, into acetic acid ($C_2H_4O_2$).

Sulphuric acid combines with dilute alcohol to form ethyl-sulphuric acid ($C_2H_5)HSO_4$. When sulphuric anhydride acts on anhydrous alcohol, a white substance called ethionic oxide is formed ($C_2H_4S_2O_6$), which, when dissolved in water, forms ethionic acid ($C_2H_6S_2O_7$).

When alcohol is allowed to act on fused potassic hydrate, hydrogen is evolved and potassic acetate is formed. Thus—

KHO	+	$C_2H_5(OH)$	=	$KC_2H_3O_2$	+	$2H_2$.
Potassic hydrate	+	Alcohol	=	Potassic acetate	+	Hydrogen.

(3.) Propylic Alcohol, $C_3H_7(OH)$.—This alcohol exists in two isomeric modifications, viz., *a normal primary propylic alcohol*, termed *ethyl carbinol*, and a *secondary isopropylic alcohol*, called *dimethyl carbinol*. These may be figured as follows—

Normal propylic alcohol (primary).	Isopropylic alcohol (secondary).
$=C_2H_5.CH_2.OH$	$=CH(CH_3)_2OH$
	

(*a*). *Normal propylic alcohol*, or ethyl carbinol, may be prepared from ethyl alcohol (*see* General Methods, 4, page 561).

Properties.—An oily liquid, yielding propionic acid by oxidation.

(*β*.) *Isopropylic alcohol*, or dimethyl carbinol, may be prepared from acetone ($(CH_3)_2CO''$ by the action upon it of nascent hydrogen. Thus—

$(CH_3)_2CO$	+	H_2	=	$CH(CH_3)_2(OH)$.
Acetone	+	Hydrogen	=	Isopropylic alcohol.

Properties.—A colorless liquid; Sp. Gr. 0·791° F. at 15° C.; boils at 185° F. (85° C.). It does not freeze at — 4° F. (— 20° C.). It has no action on a polarized ray of light. It forms hydrates of remarkable stability. It yields, by oxidation, first (*a*), acetone; and finally (*β*), acetic acid.

(*a*.) $CH(CH_3)_2(OH)$	+	O	=	$CO(CH_3)_2$	+	H_2O.
Isopropylic alcohol	+	Oxygen	=	Acetone	+	Water.

(*β*.) $CO(CH_3)_2$	+	$2O_2$	=	CH_3CO_2H	+	CO_2	+	H_2O.
Acetone	+	Oxygen	=	Acetic acid	+	Carbonic anhydride	+	Water.

(4.) Butylic Alcohol, $C_4H_9(OH)$.—There are four isomeric modifications of this alcohol. Thus—

(*a*.) $CH_3.CH_2.CH_2.CH_2(OH)$, *propyl carbinol*, or *normal primary*

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butylic alcohol, may be prepared from butylic aldehyde by the action of nascent hydrogen. It boils at 240·8° F. (116° C.).

On oxidation it yields *normal butyric acid*—

$$C_4H_9(OH) + O_2 = C_3H_7CO(OH) + H_2O.$$
Butylic alcohol + Oxygen = Normal butyric acid + Water.

(β.) $CH(CH_3)_2CH_2(OH)$ *isopropyl carbinol*, or *iso-primary butylic alcohol*, is found in the fusel oil formed when beet sugar molasses is fermented. It boils at 228·2° F. (109° C.).

On oxidation it yields *iso-butyric acid.*

$$C_4H_9(OH) + O_2 = CH(CH_3)_2CO(OH).$$
Butylic alcohol + Oxygen = Isobutyric acid.

(γ.) $C(CH_3)(C_2H_5)H(OH)$. *Methyl ethyl carbinol*, or *secondary butylic alcohol*, is prepared by the action of moist argentic oxide on methyl-ethyl-iodo-methane, formed by distilling *erythrite* ($C_4H_6(OH)_4$), a saccharine substance, with fuming hydriodic acid. Thus—

$$C(CH_3)(C_2H_5)HI + AgHO = AgI + C(CH_3)(C_2H_5)H(OH).$$
Methyl ethyl iodo-methane + Argentic hydrate = Argentic iodide + Secondary butylic alcohol.

It is a colorless oily liquid, having a Sp. Gr. of 0·85° at 32° F. (0° C.).

On oxidation it yields, first, *methylethylketone*, and finally, *acetic acid.*

(δ.) $C(CH_3)_3OH$.—*Trimethylcarbinol*, or *tertiary butylic alcohol*, is prepared by the action of water on the product formed by the action of acetic chloride on zincic methide. It boils at 180·5° F. (82·5° C.).

On oxidation it yields isobutyric, acetic and formic acids; also acetone, isobutylene, carbonic anhydride, and water.

(5.) Amylic Alcohol ($C_5H_{11}(OH)$).—There may be as many as eight isomeric modifications of this alcohol, five of which are known.

The ordinary amylic alcohol, or iso-amylic alcohol (isobutyl carbinol), is the fusel oil of the distiller. It is said to be a mixture of two different alcohols, one rotating a ray of polarized light to the left, and boiling at 262·4° F. (128° C.), the other without polar action, and boiling at 266° F. (130° C.). Amylic alcohol is an oily liquid, having a Sp. Gr. 0·8111. It imparts a transient greasy stain to paper.

On oxidation both the varieties named above, yield valeric acid.

$$C_4H_9(CH_2)OH + O_2 = C_4H_9.CO(OH) + H_2O.$$
Amylic alcohol + Oxygen = Valeric acid + Water.

Vinylic Series.

SERIES II.—*Formula* $C_nH_{2n-1}OH$.

The relationship between the vinylic series and the olefines, is identical to that subsisting between the ethylic series of alcohols and the paraffins. Thus:—

(α.) *Paraffin; Methane* CH_4 and $CH_3(OH)$ *methylic alcohol.*

(β.) *Olefine; Ethylene* C_2H_4 and $C_2H_3(OH)$ *vinylic alcohol.*

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This series includes—

1. Vinylic alcohol	$C_2H_3(OH)$
2. Allylic alcohol	$C_3H_5(OH)$

(1.) Vinylic Alcohol ($C_2H_3(OH)$).—It is prepared (α) by first combining acetylene with sulphuric acid, and (β) afterwards distilling the product with water.

(α.) C_2H_2 + H_2SO_4 = $(C_2H_3)HSO_4$.
Acetylene + Sulphuric acid = Sulphovinylic acid.

(β.) $(C_2H_3)HSO_4$ + H_2O = H_2SO_4 + $C_2H_3(OH)$.
Sulphovinylic acid + Water = Sulphuric acid + Vinylic alcohol.

It is a pungent liquid, isomeric with aldehyde and ethylenic oxide.

(2.) Allylic Alcohol ($C_3H_5(OH)$). [*Specific gravity at* 32° F. (0° C.) 0·8709. *Boiling point*, 204·8° F. (96° C.).]

Preparation.—It may be formed from glycerin, as follows:—

(1.) (α.) *Allylic iodide* (C_3H_5I) is first formed by the action of phosphorus iodide on glycerin—

$2(C_3H_5(OH)_3)$ + P_2I_4 = $2C_3H_5I$ + $2H_3PO_3$ + I_2.
Glycerin + Phosphorus iodide = Allylic iodide + Phosphorous acid + Iodine.

(β.) *Allylic oxalate* is then formed by the action of argentic oxalate on allylic iodide—

$2C_3H_5I$ + $Ag_2C_2O_4$ = $2AgI$ + $(C_3H_5)_2C_2O_4$.
Allylic iodide + Argentic oxalate = Argentic iodide + Allylic oxalate.

(γ.) *Allylic alcohol* (+oxamide) is then formed by the action of ammonia on the allylic oxalate—

$(C_3H_5)_2C_2O_4$ + $2NH_3$ = $2(C_3H_5(OH))$ + $N_2(C_2O_2)''H_4$
Allylic oxalate + Ammonia = Allylic alcohol + Oxamide.

(2.) By the action of heat on a mixture of glycerin and oxalic acid.

$C_3H_5(OH)_3$ + $C_2H_2O_4$ = $2H_2O$ + $2CO_2$ + $C_3H_5(OH)$.
Glycerine + Oxalic acid = Water + Carbonic anhydride + Allylic alcohol.

Properties.—A colorless liquid. Sp. Gr. 0·8709. Boils at 204·8° F. (96° C.). It is combustible and soluble in water in all proportions.

Its reactions resemble those of ethylic alcohol.

With *the haloids* it forms both derivatives, such as C_3H_5Br, etc., and compounds such as $C_3H_5Cl_2(OH)$. With *sulphuric acid* it forms allylic sulphuric acid, $(C_3H_5)HSO_4$. With the *alkaline metals* it forms substitution products. *Nascent hydrogen* has no action upon it. By *oxidation* it yields acrolein, formic acid and carbonic anhydride.

The *allylic sulphide* constitutes the oil of garlic [$(C_3H_5)_2S$], and is formed by acting on allylic iodide with potassic sulphide (α). Oil of

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mustard contains *allylic sulphocyanate*, and is formed artificially by the action of potassic sulphocyanate on allylic iodide (β).

(α.) $2C_3H_5I + K_2S = 2KI + (C_3H_5)_2S$.
Allylic iodide + Potassic sulphide = Potassic iodide + Allylic sulphide (garlic oil).

(β.) $C_3H_5I + KNCS = KI + (C_3H_5)(NCS)$.
Allylic iodide + Potassic sulphocyanate = Potassic iodide + Allylic sulphocyanate (mustard oil).

SERIES III.—*Formula* $C_nH_{2n-3}(OH)$.

This includes—

Propargylic Alcohol ($C_3H_3(OH)$). [*Specific gravity*, 0·9628 *at* 68°F. (20° C.). *Boils at* 239° F. (115° C.).]

Preparation.—By the action of potassic hydrate on mono-brom-allylic alcohol—

$C_3H_4Br(OH) + KHO = C_3H_3(OH) + KBr + H_2O$
Monobromallylic alcohol + Potassic hydrate = Propargylic alcohol + Potassic bromide + Water.

Properties.—A colorless mobile liquid.

Benzylic Series—The Phenols.

SERIES V.—*Formula* $C_nH_{2n-7}(OH)$.

These alcohols may be divided into two classes :—

I. Benzylic Series (normal alcohols).			Boiling Point.		Melts at	
Alcohols.	Formula.	Specific Gravity.	°F.	°C.	°F.	°C.
1. Benzylic	$C_7H_7(OH)$	1·051 at 14° C.	403·7	206·5		
2. Xylilic (toluylic) ..	$C_8H_9(OH)$		422·6	217·0	139·1	59·5
3. Cumilic	$C_{10}H_{13}(OH)$		469·4	243·0		
4. Sycocerylic	$C_{18}H_{29}(OH)$				194·0	90·0
II. Phenols.						
1. Phenylic	$C_6H_5(OH)$	1·068	356	180	95·0	35·0
2. Cresylic	$C_6(CH_3)H_4(OH)$		383—392	195—200		
3. Phlorol	$C_6(C_2H_5)H_4(OH)$	1·037 at 12° C.	374—392	190—200		
4. Dimethyl phenylic (xylenol)	$C_6(CH_3)_2H_3(OH)$		410	210		
5. Thymylic	$C_6(C_2H_5)_2H_3(OH)$		428	220	111·2	44·0

These alcohols are derivatives of the C_nH_{2n-6} series of hydrocarbons, by the substitution of a semi-molecule of hydroxyl for one atom of hydrogen.

They form well-marked substitution compounds when acted on by

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chlorine, nitric acid, etc., but they never form additive compounds; for like the hydrocarbons, from which they are derived, they are fully saturated bodies.

The haloid acids are without action on them, whilst with sulphuric acid they yield sulphonic acids, which, by fusion with potassic hydrate, are convertible into dihydric alcohols.

It will be noted that all the series of alcohols preceding the phenols, differ strikingly in these respects from the phenols. (α.) They neither form substitution compounds under the same circumstances, nor with the same ease, as the phenols. (β.) With the haloid acids they form derivatives, and (γ) with sulphuric acid they form acid ethereal salts, which, when treated with water, re-produce sulphuric acid and the alcohol.

Lastly, the products of the oxidation of the phenols and of the alcohols of the preceding series, are completely different.

Preparation.—(1.) *From the benzenes* (C_nH_{2n-6}). The conversion may be effected in one of two ways :—

(A.) By first acting on the hydrocarbon with sulphuric acid, and afterwards fusing the potassic salt of the monosulphonic acid formed, with potassic hydrate.

(B.) By the action of nitrous acid on the amido-derivative of the hydrocarbon.

Benzylic Alcohol (C_7H_7OH or $C_6H_5(CH_2)OH$). [*Specific gravity*, 1·051 *at* 14° C. *Boils at* 206·5° C.]

Preparation.—(1.) By the action of alcoholic potassic hydrate on benzoic aldehyde (oil of bitter almonds)—

$2C_6H_5COH$	+	KHO	=	$C_7H_7(OH)$	+	$K(C_7H_5O)O$.
Benzoic aldehyde	+	Potassic hydrate	=	Benzylic alcohol	+	Potassic benzoate.

(2.) *From toluene.* By the action of potassic hydrate on toluylic chloride.

C_7H_7Cl	+	KHO	=	$C_7H_7(OH)$	+	KCl.
Toluylic chloride	+	Potassic hydrate	=	Benzylic alcohol	+	Potassic chloride.

(3.) By the action of nascent hydrogen on benzoic or hippuric acids.

Properties.—A colorless, oily, highly refracting liquid, insoluble in water, but soluble in all proportions in alcohol, ether, acetic acid, and carbonic disulphide. With *hydrochloric acid* it forms benzylic chloride, $C_6H_5.CH_2.Cl$. With *strong sulphuric acid* it forms a resinous body. Distilled with sulphuric and acetic acids, it forms benzyl acetate ($C_7H_7(OC_2H_3O)$), a liquid having a pear odor. By *oxidation with nitric acid* it forms benzoic aldehyde, and with *chromic acid* benzoic acid.

Phenylic Alcohol ($C_6H_5(OH)$).—[*Molecular weight*, 94. *Molecular volume* [ ]. *Specific gravity*, 1·065 *at* 64·4° F. (18° C.). *Fuses at* 93·2° F. (34° C.). *Boils at* 370·4° F. (188° C.). 100 c. i. *of vapor weigh* 32·945 grms., *and* 1 litre 4·211 grms.].

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Synonyms.—Carbolic acid; Phenylic acid; Phenic acid; Oxy-benzene; Phenol; Coal tar Kreasote.

Natural History.—It is found in the urine of cows and other animals.

Preparation.—(1.) By the action of nitrous acid on amidobenzene (aniline). Thus :—

$$C_6H_5(NH_2) + HNO_2 = C_6H_5(OH) + H_2O + N_2.$$

Aniline + Nitrous acid = Phenylic alcohol + Water + Nitrogen.

(2.) By distilling salicylic acid either alone or mixed with lime, etc.

$$C_7H_6O_3 = C_6H_5(OH) + CO_2.$$

Salicylic acid = Phenylic alcohol + Carbonic anhydride.

(3.) (*Commercial preparation.*) The dead oil of coal tar is first distilled, that portion which passes over between 300° and 400° F. (149° and 205° C.) being collected separately. This is shaken up with a hot concentrated solution of sodic hydrate, which dissolves the carbolic acid, and enables it to be separated from the oil that floats on the surface. The alkaline solution is then decomposed with hydrochloric acid, when the carbolic acid separates as an oily layer on the surface. This is drawn off, digested with calcic chloride to remove the water, and distilled. By exposing the distilled acid to a low temperature it solidifies. The crystals are collected, drained, and again distilled.

Sometimes the dead oil (without distillation) is treated with a mixture of slaked lime and water, and the solution which contains the carbolic acid, drawn off from the oil which swims on the surface.

Tests for the purity of carbolic acid—

(1.) Shake up half a dram of the acid with half a pint of warm water. The acid is perfectly soluble in the water, whilst any dead oil present as an impurity of the acid will float on the surface.

(2.) Five parts of pure carbolic acid are soluble in a mixture of one part of caustic soda and ten parts of water.

(3.) Expose a mixture of carbolic acid (3 parts by weight) and water (1 part) to the cold of ice, when crystals are deposited having the formula $2C_6H_6O.H_2O$ soluble in alcohol, in ether and in water. The crystals melt at 61° F. (16·1° C.).

To *distinguish carbolic acid from kreasote* (the product of wood)—

Carbolic Acid.	Kreasote.
1. Boils at 370° F. (187·8° C.)	1. Dries up at 212° F. (100° C.).
2. Does not affect a polarized ray.	2. Rotates a polarized ray to the right.
3. Is solidified by cooling.	3. Not solidified by ice and salt.
4. Forms a jelly when shaken with collodion.	4. Is unaffected by collodion.
5. Is soluble in a strong solution of ammonia or potassic hydrate.	5. Is insoluble in ammonia or in potassic hydrate solutions.
6. Solubility in water; 1 in 20 at 212° F.; 1 in 80 at 60° F.	6. Solubility in water; 1 in 130 at 60° F.
7. Ferric chloride turns the aqueous solution blue.	7. Solution not colored blue by ferric chloride.
8. Ferric chloride turns the solution in alcohol brown.	8. Ferric chloride turns the solution in alcohol green.

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Properties.—(α.) *Physical.* Carbolic acid when pure, crystallizes in colorless needles which are very deliquescent, and melt at 93·2° F. (34° C.), forming an oily liquid, which boils at 370·4° F. (188° C.). It has a specific gravity at 18° C. of 1·065. Its odor is peculiar, and its action caustic. It is not easily decomposed even by a red heat. Distilled over heated zinc dust, it yields benzene. It is slightly soluble in water, but is very soluble in alcohol and in ether, and is a solvent of sulphur, iodine, etc. Its special action is antiseptic.

Its appearance to the naked eye closely resembles kreasote, from which it may be known by the tests already described.

(β.) *Chemical.* Its solution is not acid to litmus. *The haloid* elements form with it substitution compounds (as $C_6H_3Cl_2(OH)$ and $C_6Cl_5(OH)$ *pentachlorophenol*). With *nitric acid* it forms $C_6H_4(NO_2)OH$, $C_6H_3(NO_2)_2OH$, and finally the substitution product $C_6H_2(NO_2)_3(OH)$, or *picric acid.* All its nitro derivatives decompose the metallic carbonates. With *sulphuric acid* it forms phenol disulphonic acid, $C_6H_3OH(SO_3H)_2$. The *haloid acids* are without action upon it. The *alkalies* (but not the alkaline carbonates) dissolve it, forming phenates. By *oxidation* with chromic acid it yields phenoquinone.

$$\underset{\text{Phenylic alcohol}}{3[C_6H_5(OH)]} + O_3 + H_2O = \underset{\text{Pheno-quinone.}}{C_6H_4(O.OC_6H_5)_2} + 3H_2O.$$

Cresylic Alcohol (*cresol*) $C_6H_4(CH_3)OH$.—This occurs in three modifications, which yield three isomeric cresol-sulphonic acids.

(α.) *Paracresol* is a solid crystalline body, boiling at 392° F. (200° C.). When fused with potassic hydrate, paracresol yields *potassic paroxybenzoate,* $C_6H_4(OH)CO_2K$.

(β.) *Metacresol* is a liquid, and boils at 392° F. (200° C.). When fused with potassic hydrate, metacresol yields *potassic metoxybenzoate.*

(γ.) *Orthocresol* is a liquid, and boils at 372·2° F. (189° C). When fused with potassic hydrate, orthocresol yields *potassic salicylate* (orthoxybenzoate).

Thymylic Alcohol $C_6(C_2H_5)_2H_3(OH)$.—The thymols exist in two isomeric forms. *Thymol* (α) is found in the oil of thyme and other plants. It is a crystalline solid, melting at 111·2° F. (44° C.), and boiling at 428° F. (220° C.). By the action of sulphuric acid it is completely converted into a sulpho-acid. *Thymol* (β) is a yellow viscid oil which, by the action of sulphuric acid, is only very partially converted into a sulpho-acid.

SERIES VI.—*Formula* $C_nH_{2n-9}(OH)$.

This includes—

Cinnamic alcohol.	$C_9H_9(OH)$	*Preparation.*—By heating styracin with potassic hydrate. With *nascent hydrogen* it forms phenylpropylic alcohol and allyl benzene. By *oxidation* it yields cinnamic aldehyde. Melting point, 91·4° F.; 33° C.
Cholesterin ..	$C_{26}H_{43}(OH)$	A crystalline solid, present in different parts of the animal. It forms, by oxidation with chromic acid, oxycholic acid, $C_{26}H_{40}O_6$.

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B.—DIHYDRIC ALCOHOLS.

The Glycols.

SERIES I.—*Formula* $C_nH_{2n}(OH)_2$.

This series includes—

Glycols.	Formula.	Boiling Point.	
		° F.	° C.
Ethylene glycol	$C_2H_4(OH)_2$	387·5	197·5
Propylene ,, ...	$C_3H_6(OH)_2$	370·4—372·2	188—189
Butylene ,, ...	$C_4H_8(OH)_2$	361·4—363·2	183—184
Amylene ,, ...	$C_5H_{10}(OH)_2$	350·6	177
Hexylene ,, ...	$C_6H_{12}(OH)_2$	404·6	207
Octylene ,, ...	$C_8H_{16}(OH)_2$	455—464	235—240

The glycols (or diatomic alcohols) may be regarded (1) *as derivatives of the paraffins*, where two atoms of hydrogen are replaced by two semi-molecules of hydroxyl (OH). Thus—

Ethane C_2H_6 forms $C_2H_4(OH)_2$, *glycol.*

Propane C_3H_8 ,, $C_3H_6(OH)_2$, *propylene glycol*, etc.,

Or (2) they may be regarded as *compounds of the olefines* with hydroxyl. Thus—

Ethylene C_2H_4 + $(OH)_2$ forms $C_2H_4(OH)_2$, *ethylene glycol.*

Propylene C_3H_6 + $(OH)_2$,, $C_3H_6(OH)_2$, *propylene glycol*, etc.

Preparation.—From the olefines. We may illustrate this in the preparation of glycol :—

(*α.*) A *dibromide* ($C_2H_4Br_2$) is first formed by the action of bromine on ethylene :—

(*β.*) A *diacetate of the olefine* is now formed, by the action of argentic or potassic acetate on the dibromide. Thus :—

$C_2H_4Br_2$	+	$2AgC_2H_3O_2$	=	$2AgBr$	+	$C_2H_4(C_2H_3O_2)_2$.
Ethylene dibromide	+	Argentic acetate	=	Argentic bromide	+	Ethylenic diacetate.

(*γ.*) A *glycol* (+potassic acetate) is now formed, by treating the diacetate with potassic hydrate. Thus :—

$C_2H_4(C_2H_3O_2)_2$	+	$2KHO$	=	$2KC_2H_3O_2$	+	$C_2H_4(OH)_2$
Ethylenic diacetate	+	Potassic hydrate	=	Potassic acetate	+	Glycol.

Properties.—(*α.*) *Physical.* Ethylene glycol (commonly called *glycol*) is the only member of the series that has been particularly studied. The glycols are colorless liquids, without odor, freely soluble in water and in alcohol, and also (excepting ethylene glycol) in ether.

(*β.*) *Chemical.* The reactions of the glycols are similar to those of the monatomic alcohols, excepting in this, that having two semi-molecules of replaceable hydroxyl, two series of products result.

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With sodium and potassium the glycols form two substitution products. Thus:—

$C_2H_4(HO)(NaO)$; Monosodic glycol; $C_2H_4(NaO)_2$. Disodic glycol.

These compounds form the alcoholic ethers of the glycols when treated with a monatomic alcoholic iodide. Thus:—

$C_2H_4(OH)(ONa)$	+	C_2H_5I	=	NaI	+	$C_2H_4(C_2H_5O)(OH)$.
Monosodic glycol	+	Ethylic iodide	=	Sodic iodide	+	Ethylic ethynate.

Oxygen acids form with the glycols, ethereal salts, which are mono- or di-acid, according to the proportions of the reagents respectively used. The *haloid acids* and haloid phosphorus compounds form with them mono- and di-haloid derivatives. *Potassic hydrate*, when heated with glycol, forms potassic oxalate ($C_2H_4(OH)_2+2KHO=C_2O_2(OK)_2+4H_2$). By *oxidation* glycol yields (α) first glycolic acid (other acids, varying with the glycol acted upon, being formed), and finally (β) oxalic acid.

(α.)	$C_2H_4(OH)_2$	+ O_2	=	$CH_2(OH)CO(OH)$	+	OH_2.
	Glycol	+ Oxygen	=	Glycollic acid	+	Water.
(β.)	$CH_2(OH)CO(OH)$	+ O_2	=	$C_2O_2(OH)_2$	+	H_2O.
	Glycollic acid	+ Oxygen	=	Oxalic acid	+	Water.

We may here note that the relationship between ethylic alcohol, ethylic aldehyde, and acetic acid, finds its counterpart in that subsisting between glycol, glyoxal (glycolic aldehyde), and oxalic acid. Thus:—

$CH_3.CH_2(OH)$, Ethylic alcohol; CH_3COH, Aldehyde; $CH_3.CO(OH)$; Acetic acid;

$CH_2(OH).CH_2(OH)$, Glycol; $COH.COH$, Glyoxal; $CO(OH)CO(OH)$. Oxalic acid.

Between glycol and ethylic alcohol this point of difference is to be noted,—that whereas *alcohol* forms only *one* substitution compound with sodium, sulphuric acid, etc., *glycol* forms *two*. Thus:—

Alcohol forms—	*Glycol forms*—
$C_2H_5(ONa)$,	$C_2H_4(OH)(ONa)$ and $C_2H_4(ONa)_2$,
$C_2H_5(HSO_4)$;	$C_2H_4(OH)(HSO_4)$ and $C_2H_4(HSO_4)_2$.

By heating glycol with ethylenic oxide in sealed tubes, a series of compounds called *polyethylenic glycols* (or *alcohols*) are formed. They are the result of progressive condensation (although normal condensation to two volumes) with elimination of the elements of water. They are syrupy liquids, diethylenic glycol boiling at 473° F. (245° C.), each succeeding term of the series boiling at about 81 degrees Fahrenheit (45° C.) higher than the one below it. The following compounds are known:—

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Alcohol.	Formula.
Diethylenic glycol	$C_4H_{10}O_3 = 2C_2H_4(OH)_2 - H_2O$
Triethylenic ,, ...	$C_6H_{14}O_4 = 3C_2H_4(OH)_2 - 2H_2O$
Tetrethylenic ,, ...	$C_8H_{18}O_5 = 4C_2H_4(OH)_2 - 3H_2O$
Pentethylenic ,, ...	$C_{10}H_{22}O_6 = 5C_2H_4(OH)_2 - 4H_2O$
Hexethylenic ,, ...	$C_{12}H_{26}O_7 = 6C_2H_4(OH)_2 - 5H_2O$

Orcins—Aromatic Glycols—Saligenin Series.

SERIES II.—*Formula* $C_nH_{2n-8}(OH)_2$.

This series, the members of which are derivatives of benzene, include—

Alcohol.	Formula.	Melting Pt.		Preparation, Properties, etc.
		° F.	° C.	
Hydroquinone..	$C_6H_4(OH)_2$	351·5	177·5	*Preparation.*—By the dry distillation of quinic acid. By oxidation it forms quinone.
Resorcin	Ditto	210·2	99·0	*Preparation.*—By fusing resin of galbanum or benzene disulphonic acid with potassic hydrate. Soluble in water, alcohol, and ether. Aqueous solutions give a violet with Fe_2Cl_6, and reduce $AgNO_3$. Forms substitution compounds.
Pyrocatechin .. (oxyphenol)	Ditto	232·7	111·5	*Preparation.*—By the distillation of catechin, etc., and by the action of alkalies on meta-iodophenol. With Fe_2Cl_6 gives a dark green color, and with plumbic acetate a white precipitate.
Orcin	$C_6H_3(CH_3)(OH)_2$	186·8	86·0	Found in the lichens used for the preparation of cudbear, litmus, etc. May be formed artificially. By the action of ammonia and free oxygen, it forms orcein ($C_7H_7NO_3$?), the coloring matter of archil and cudbear. It forms numerous substitution products with the haloids and with nitric acid.
Salicylic alcohol (saligenin)	$C_6H_4(OH)CH_2(OH)$	179·6	82·0	*Preparation.*—By the decomposition of salicin under the influence of a ferment as synaptase, or of dilute sulphuric acid. By oxidation it yields salicylic aldehyde, $C_6H_4(OH)COH$. With ferric salts, its aqueous solution gives an indigo blue coloration.

C.—TRIHYDRIC ALCOHOLS.

Glycerin Series.—SERIES I. *Formula* $C_nH_{2n-1}(OH)_3$.

This includes—

Glycerin ... ... $C_3H_5(OH)_3$.
Amylglycerin ... ... $C_4H_7(OH)_3$.

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Glycerin.—($C_3H_5(OH)_3$ = $C(CH_2.OH)_2H.OH$.) [*Specific gravity at* 60° F. (15·5° C.), 1·27. *Boils at* 355·1° F. (179·5° C.)]

Synonym.—Propenyl alcohol.

Natural History.—It occurs in most animal and vegetable fats in combination with the acids of the acetic and oleic series, that is, as glycerides or ethereal salts. Olive oil, for example, contains *olein*, or a *glyceride of oleic acid;* suet contains *stearin*, or a *glyceride of stearic acid;* palm oil contains *palmitin*, or *a glyceride of palmitic acid.* From these bodies glycerin is usually prepared as a bye product in the manufacture of soap and candles.

Preparation.—(1.) By the action on fats of superheated steam.

$C_3H_5(C_{18}H_{35}O_2)_3$	+	$3H_2O$	=	$C_3H_5(OH)_3$	+	$3C_{18}H_{36}O_2$.
Stearin	+	Water	=	Glycerin	+	Stearic acid.

Thus, glycerin may be prepared by merely distilling the fat with superheated steam (see *Saponification by steam*), when decomposition occurs, and the distillate, on standing, separates into two parts, the fatty acids floating on the surface of the glycerin.

(2.) By the action of a base on fats (saponification). (*See* Soaps, Candles, etc.)

$C_3H_5(C_{18}H_{35}O_2)_3$	+	3NaHO	=	$C_3H_5(OH)_3$	+	$3C_{18}H_{35}NaO_2$.
Stearin	+	Sodic hydrate	=	Glycerin	+	Sodic stearate.

The glycerin solution, or spent lye as it is called, (the stearate having been first rendered insoluble by the addition of sodic chloride,) is drawn off, and distilled in a current of superheated steam. The water is removed from the distillate by evaporation.

Glycerin is formed in small quantity during the fermentation of sugar.

(3.) Glycerin may be prepared synthetically, by digesting trichlorhydrine ($C_3H_5Cl_3$), a compound formed by heating together propylene and iodine chlorides with water in closed tubes at 338° F. (170° C.)

$C_3H_5Cl_3$	+	$3H_2O$	=	$C_3H_5(OH)_3$	+	3HCl.
Trichlorhydrine	+	Water	=	Glycerin	+	Hydrochloric acid.

Properties.—(*a.*) *Physical.* A viscid liquid without color or smell. It has a sweet taste. Specific gravity 1·27.

Action of heat.—At ordinary pressure glycerin cannot be distilled without undergoing decomposition, darkening in color, and evolving (amongst other products) acrolein. When however it is distilled, either in vacuo at 410° F. (210° C.), or in an atmosphere of steam, it passes over undecomposed. It is soluble in water in all proportions.

(*β.*) *Chemical.*—It has no reaction on red or blue litmus, or upon any vegetable colouring matter. A solution of glycerin with yeast does not undergo vinous fermentation, but is gradually converted into propionic acid ($C_3H_8O_3$ = $C_3H_6O_2$ + H_2O). By the action of *dehydrating agents* it forms acrolein ($C_3H_8O_2$ = $2H_2O$ +

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C_3H_4O). It combines with sulphuric acid to form sulpho-glyceric acid ($C_3H_8O_3SO_3$), which forms soluble salts with lime and baryta. With a mixture of strong nitric and sulphuric acids it forms *nitro-glycerin*, or *glonoin* (*Nobel's blasting oil*), ($C_3H_5(OH)_3 + 3HNO_3 = 3H_2O + C_3H_5(NO_3)_3$), an oily and highly explosive liquid (*Specific gravity* 1·6). The monatomic *organic acids*, such as glacial acetic acid, when heated with it in closed tubes, form glycerides or glyceric ethers, as mon-, di-, or tri-acetin, as *e.g.*, monacetin, $C_3H_5(OH)_2(C_2H_3O_2)$. *Hydrochloric and hydrobromic acids* or the *compounds of phosphorus with chlorine or bromine*, form substitution compounds with glycerine, called mono-, di-, or tri-chlorhydrins or bromhydrins, where the group OH is replaced by chlorine or bromine; as *e.g.*, *Monochlorhydrine*, $C_3H_5Cl(OH)_2$, etc.

[Monochlorhydrine by the action of nascent hydrogen forms propylic glycol, $C_3H_6(OH)_2$.]

Hydriodic acid or phosphorus iodide forms with glycerin, isopropylic iodide (C_3H_7I) and allylic iodide (C_3H_5I). By slow *oxidation* with nitric acid, glycerin forms glyceric acid ($C_3H_8O_3 + O_2 = C_3H_6O_4 + H_2O$), and by the further action of the acid oxalic acid ($C_2H_2O_4$), which containing as it does fewer carbon atoms than glyceric acid, is clearly to be regarded as the result of its decomposition.

Pyrogallic Series.

SERIES II.—*Formula* $C_nH_{2n-9}(OH)_3$.

These alcohols, like the phenyls and orcins, are direct derivatives of benzene.

This series includes:—

	Formula.	Melting point.	
		° F.	° C.
Pyrogallol	$C_6H_3(OH)_3$	239	115
Phloroglucin	ditto	248	120

Pyrogallol ($C_6H_3(OH)_3$) (*Pyrogallic acid*). Melts at 239° F. (115° C.). Boils at 410° F. (210° C.).

Preparation.—By the action of heat on gallic acid.

$C_6H_2(OH)_3CO_2H$	=	$C_6H_3(OH)_3$	+	CO_2.
Gallic acid	=	Pyrogallic acid	+	Carbonic anhydride.

Properties.—A crystalline body, soluble in water, alcohol, and in ether. It does not neutralize alkalies, nor does it form true salts. It decomposes at 482° F. (250° C.), leaving a residue of metagallic acid ($C_6H_4O_2$). When dissolved in a strong potassic hydrate solution, it rapidly

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absorbs free oxygen (*see* page 98). With *pure* ferrous salts it forms a fine blue color. Distilled at a red heat over zinc dust, it yields benzene.

E.—HEXHYDRIC ALCOHOLS.

Formula $C_nH_{2n-4}(OH)_6$ Series.

This includes the two natural sugars mannite and dulcite.

Mannite, $C_6H_8(OH)_6$. *Natural History.*—It is found in manna, (the sap derived from different species of ash; Fraxinus ornus), and also in other plants, such as seaweed, mushrooms, etc.

Preparation.—(1.) By the action of boiling alcohol on manna.

(2.) By the action of nascent hydrogen (sodium amalgam) on an aqueous solution of glucose.

Properties.—Mannite crystallises in four-sided crystals, which are sweet to the taste, soluble in water and in alcohol, and insoluble in ether.

It does not ferment, thus differing from cane-sugar. It has no action on polarised light, nor does it reduce an alkaline solution of cupric hydrate on boiling, thus differing from grape-sugar.

Its relationship to the alcohols, and its hexatomic character, is marked as follows:—(1.) By the action of nitric acid and of stearic acid $[C_{18}H_{35}O(OH)]$ it forms *nitromannite* and *mannite hexastearate* respectively, six hydrogen atoms in these compounds being replaced by six of the group (NO_2), or by six of the radical of stearic acid $(C_{18}H_{35}O)$. Thus:—

$C_6H_8(OH)_6$;	$C_6H_8(ONO_2)_6$;	$C_6H_8(OC_{18}H_{35}O)_6$.
Mannite ;	Nitro mannite ;	Mannite hexastearate.

(2.) With *hydriodic acid* it forms *iodohexane* ($C_6H_{13}I$), from which, by the action of argentic oxide and water, normal secondary hexylic alcohol may be obtained.

(3.) *By oxidation* (as by the action of platinum black) it yields *mannitic acid*, $C_6H_{12}O_7$, and (by the action of dilute nitric acid) *saccharic acid*, $C_6H_{10}O_8$.

Dulcite ($C_6H_8(OH)_6$) closely resembles its isomer mannite. *Naturally*, it is obtained from the expressed juice of the melampyrum nemorosum; *artificially*, it is prepared by the action of nascent hydrogen on inverted milk-sugar.

By oxidation with nitric acid it forms *mucic acid*, an isomer of saccharic acid.

Mercaptans or Thio-Alcohols.

The relationship subsisting between *potassic hydrate* (KHO) and *potassic sulphydrate* (KHS), has its counterpart in the relationship between

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an alcohol, as *ethylic alcohol* ($C_2H_5(OH)$), and a mercaptan or thio-alcohol, as *ethylic sulphydrate* ($C_2H_5(SH)$). The name *mercaptan* was originally applied solely to ethylic sulphydrate the first discovered of these compounds, but it is now applied to the whole class of like bodies.

Preparation.—(1.) From *the corresponding alcohols* by distillation with phosphorus pentasulphide:—

$5[C_2H_5(OH)]$	+	P_2S_5	=	$5[C_2H_5(SH)]$	+	P_2O_5.
Ethylic alcohol	+	Phosphorus pentasulphide	=	Ethylic sulphydrate	+	Phosphoric anhydride.

(2.) From *certain hydrocarbons;* by acting upon their haloid derivatives with potassic sulphydrate. Thus:—

CH_3Cl	+	KHS	=	$CH_3(HS)$	+	KCl.
Methylic chloride	+	Potassic sulphydrate	=	Methylic sulphydrate	+	Potassic chloride.

The mercaptans are mostly offensive-smelling liquids, but some are solid. By the action upon their alcoholic solutions of certain *metals* (as K and Na), or of certain *metallic oxides* (as HgO) or *salts* (as $HgCl_2$), the mercaptans form stable crystalline metallic derivatives, as *e.g.*, *potassic mercaptide*, ($C_2H_5(KS)$, *mercuric mercaptide* ($C_2H_5)_2(Hg''S_2)$ etc. *By oxidation with nitric acid,* the mercaptans form sulphonic acids.

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SUPPLEMENTARY CHAPTER TO THE ALCOHOLS.

CARBO-HYDRATES.

The sugars, gums, starches, etc., are called carbo-hydrates, inasmuch as combined with carbon they contain hydrogen and oxygen in the proportions to form water. They may be arranged as follows:—Those that rotate a ray of polarised light to the right are marked +, and those that rotate it to the left —.

Group I.—Sucroses: *Composition* $C_{12}H_{22}O_{11}$.

1. Cane or sparkling sugar (sucrose) +.
2. Milk sugar (lactose) +.
3. Melitose —. 4. Melizitose —. 5. Trehalose —. 6. Mycose +.

Group II.—Glucoses: *Composition* $C_6H_{12}O_6$.

1. Grape sugar (dextrose) +.
2. Fruit or mucoid sugar (lævulose) —.
3. Galactose +.
4. Sorbite +. 5. Eucalyn +. 6. Inosite 0.

Group III.—Amyloses: *Composition* $(C_6H_{10}O_5)_n$.

1. Starch +.
2. Dextrin +.
3. Gums.
4. Cellulin.

GROUP I.—THE SUCROSES.

Formula $C_{12}H_{22}O_{11}$.

(1.) Cane or Sparkling Sugar ($C_{12}H_{22}O_{11}$).—*Sucrose.*

Natural History.—It is only found in the vegetable kingdom, as *e.g.*, in the *sugar-cane* (saccharum officinarum), to the extent of 20 per cent.; the *Asiatic sugar-cane* (sorghum saccharatum), 9·5 per cent.; the *maple* (acer saccharinum), 5 per cent.; the *white beet*, 7 to 11 per cent.; the *date palm* (saguerus saccharifer); and maize (7·5 per cent.)

Probably sucrose is present in all plants just before flowering, at which time the soluble nutriment of the plant is most abundant.

Preparation.—(1.) The juice is first expressed from the plant. This

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is effected by *rollers* in the case of the sugar-cane, by *cutting* in the case of the beet, by *tapping* in the case of the maple, etc.

(2.) The free acid of the juice is as soon as possible after extraction neutralized with lime, and heated to 140° F. (60° C.). A coagulum separates, containing albumen, earthy phosphates, etc. There must be *no delay* in this part of the process, otherwise the albumen present in the juice would set up fermentation, and cause a loss of sugar. The free acid *must be neutralised* with lime before boiling, otherwise it would, on boiling, convert a portion of cane into grape sugar, and so cause loss.

(3.) The clear liquor is now evaporated in open pans. (No doubt the large quantity of molasses formed is greatly due to this part of the operation.)

(4.) It is now crystallised in open wooden troughs, and at the same time briskly stirred, to prevent the formation of large crystals. The solid sugar formed, is separated in casks with perforated bottoms from the uncrystallisable syrup. The former, dried in the sun, constitutes *raw* or *Muscovado sugar* (foots), and the latter *molasses*.

Sugar Refining.

(1.) The raw sugar is dissolved in water, and the solution in which a little lime, some ground bone-black (4 to 100 of sugar), and albumen, such as the serum of bullock's blood has been mixed, is then boiled by steam (blow up). The albumen, as it coagulates, carries up with it the impurities suspended in the juice. The bone-black is added to assist in decolorising the solution.

(2.) The clear liquor is now further decolorised by filtration through animal charcoal.

(3.) The colorless filtrate is now evaporated "in vacuo." By this means, the boiling-point of the syrup is reduced from 230° F. (110° C.) to 150° F. (65·5° C.), that is, below the temperature at which heat injuriously affects sugar. The evaporation is continued until the syrup is sufficiently concentrated to "draw out."

(4.) The syrup is now run into coolers, and well stirred until crystallisation commences, when it is poured into moulds. After it has set, the treacle is drained off, the sugar washed with a little clean syrup in order to remove adhering coloring matters, and the solid mass finally dried and polished in a lathe. This constitutes "loaf sugar."

It may be roughly stated that the raw sugar obtained is one-tenth the weight of the original juice, that is, about one-half the quantity of sugar the juice is known to contain. The raw sugar yields about 60 per cent. of pure cane sugar, the remainder consisting of water, uncrystallisable sugar, coloring matters, etc.

Properties.—(a.) *Physical.* Sugar is a colorless and sweet body, crystallizing in oblique rhombs; Sp. Gr. 1·6. It rotates a ray of light to the right (73° 8′).

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Action of heat.—(α.) *On dry sugar.*—Sugar melts at 365° F. (185° C.), changing *without loss of weight* into a mixture of dextro-glucose and lævulose ($C_{12}H_{22}O_{11} = C_6H_{12}O_6 + C_6H_{10}O_5$). The action of this mixture on a ray of polarized light is directly opposite to that of cane sugar. Hence it is called *inverted sugar* (fruit sugar), the specific rotatory power of the lævulose being greater than the specific rotatory power of the dextro-glucose.

At from 365° to 400° F. (185° to 204·5° C.) the sugar gives off water and becomes discolored, forming "*toffy.*"

At from 400° to 420° F. (204·5° to 215·5° C.) it gives off more water, blackens, and leaves a brown residue called "*caramel*" ($C_{12}H_{18}O_9$).

Above this temperature it gives off inflammable and other gases (CO; CH_4; CO_2; etc.), and a liquid distillate consisting of acetic acid, acetone, aldehyde, and a brown oil containing furfurol and assamar. Charcoal only remains in the retort after the operation.

(β.) *On a solution of sugar in water.*—By boiling a solution of cane sugar, it becomes inverted sugar ($C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$). This change is assisted by the presence of dilute sulphuric or other mineral or organic acid, and also of certain salts. By prolonged boiling with dilute acids, brown products such as ulmine, are formed.

Heated to 365° F. (185° C.) with a very little water, sugar becomes vitreous, and solidifies to an amorphous mass, called "*barley sugar,*" which is an admixture of amorphous and crystallizable sugar. The amorphous sugar contained in barley sugar gradually becomes crystalline and opaque by keeping.

Solubility.—Sugar is soluble in cold water (1 in 2 aq. by weight), its solubility in boiling water being almost unlimited. It is almost insoluble in alcohol, and in ether. Boiling absolute alcohol dissolves $\frac{1}{80}$th part of its weight, but gives it up again on cooling.

Action of acids.—Strong mineral acids rapidly decompose it. With *sulphuric acid* the sugar is completely decomposed, carbon being separated and SO_2 evolved. This reaction is peculiar to *cane* sugar. With *nitric acid,* oxalic and saccharic acids are formed. With *hydrochloric acid,* ulmin and ulmic acid are formed. With *nitro-sulphuric acid,* an amorphous, explosive, nitro-compound is formed ($C_{12}H_{18}(NO_2)_4O_{11}$). The action of weak mineral or vegetable acids is to convert sucrose, which is non-fermentable, into dextrose and lævulose, both of which may be fermented.

Action of alkalies.—Concentrated solutions of the alkalies form with cane sugar bodies called sucrates. Dilute solutions act feebly and slowly, forming ulmic acid. Triturated with the dried caustic alkalies, it does not turn brown, thereby distinguishing it from grape sugar.

Action of oxidizing bodies.—By oxidation with sulphuric acid and manganic peroxide, sugar yields *formic acid,* but with dilute nitric acid it yields saccharic and oxalic acids. It burns vividly when a mixture

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with potassic chlorate is touched with a drop of sulphuric acid. It fires when triturated with plumbic peroxide. It reduces silver and mercury salts by heat. Pure cupric hydrate is very slowly reduced by it even when the solution is boiling, but in the presence of an alkali a blue solution is formed, which, slowly and imperfectly, precipitates cuprous oxide on boiling.

Cane sugar does not ferment directly, but it does indirectly by conversion into dextrose and lævulose.

(2.) Milk Sugar (*Lactin* or *Lactose*) $C_{12}H_{22}O_{11}$.

Natural History.—Found only in animals (milk of mammalia).

Preparation.—From the *whey* of milk by evaporation and crystallization.

Properties.—(*a.*) *Physical.* A hard gritty substance, crystallizing in square prisms. It is not very sweet. It has a specific gravity of 1·5, and rotates a ray of light + 59° 3′.

Solubility.—Soluble in water (1 in 6 at 60° F.; 1 in 2·5 at 212° F.). It is insoluble in alcohol and ether.

Action of heat.—At 284° F. (140° C.) two molecules of lactose lose one molecule of water. At 400° F. (204·5° C.) it fuses and loses more water. In other respects the action of heat upon it, corresponds to that on cane sugar.

(*β.*) *Chemical.* Milk sugar is decomposed by strong acids. Nitric acid, by oxidation, converts it into mucic, saccharic, tartaric and oxalic acids. Boiled with dilute acids, it is changed into a fermentable sugar called *galactose* ($C_6H_{12}O_6$), a body which, with nitric acid, forms mucic acid, and rotates a ray of light + 83° 3′. Lactose does not itself undergo vinous fermentation, but under the action of yeast rapidly changes to the fermentable body (galactose). Under the action of chalk and cheese it forms lactic acid, a certain quantity of alcohol being formed simultaneously. Boiled with an alkaline solution of cupric hydrate, it precipitates seven-tenths as much cuprous oxide as dextrose.

(3.) Melitose ($C_{12}H_{22}O_{11}$).—This is obtained from various species of eucalyptus. The crystals have a slightly saccharine taste. It is soluble in water (1 in 9 at 60° F.; 1 in 3 at 212° F.), and in boiling alcohol. It is dextro-rotatory 102°.

By the action upon it either of dilute sulphuric acid and heat, or of yeast, it forms two kinds of sugar, a fermentable sugar, *glucose*, and an unfermentable sugar, *eucalyn*. Nitric acid oxidizes it to mucic and oxalic acids. It does not reduce an alkaline cupric solution.

(4.) Melizitose ($C_{12}H_{22}O_{11}$) is obtained from the larch. It is dextro-rotatory 94° 1′. With nitric acid it forms oxalic acid. On boiling with dilute sulphuric acid it yields glucose. It ferments with difficulty.

(5.) Trehalose ($C_{12}H_{22}O_{11}$), is obtained from the trehala manna of Syria. It is dextro-rotatory 200°. It forms a detonating compound with strong nitric acid; with dilute nitric acid it forms oxalic acid.

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It ferments very imperfectly, and does not precipitate cuprous oxide from alkaline cupric solutions.

(6.) **Mycose** ($C_{12}H_{22}O_{11}$) is obtained from ergot, mushrooms, etc. It is dextro-rotatory 173°. It ferments slowly.

GROUP II.—THE GLUCOSES.

Formula $C_6H_{12}O_6$.

(1.) **Grape Sugar** (*Glucose; Dextrose; Dextro-Glucose; Granular Sugar*) ($C_6H_{12}O_6$).

History.—It is found both in the vegetable and animal kingdoms. (α.) In the *vegetable* kingdom it is found in fossil ferns and in vegetable mould; in sweet fruits and in honey; in chestnuts; in growing potatoes and in malt. In ripe fruits and in honey, it usually occurs together with lævulose and cane sugar.

(β.) In the *animal* kingdom it is found in the urine, in very minute quantity in health, but often in enormous quantity in diabetes. It also occurs in the liver and in the stomach during digestion.

Preparation.—(1.) From *fruits*, etc., by solution in water and precipitation with spirit. From *honey*, by washing with dilute alcohol, which dissolves the lævulose but leaves the glucose.

(2.) By the action of diastase (malt) on starch, or by merely boiling the starch in dilute sulphuric acid. The acid is to be neutralized with chalk, and the clear solution evaporated to a syrup and crystallised.

$C_6H_{10}O_5$	+	H_2O	=	$C_6H_{12}O_6$.
Starch	+	Water	=	Glucose.

Glucose is also formed by the action of dilute acids on cellulose.

(3.) By the action of dilute acids on the glucosides, such as æsculin, amygdalin, chitin, glycyrrhizin, salicin, etc.

Properties.—A granular non-sparkling body, forming nodular masses of minute acicular radiating crystals ($C_6H_{12}O_6,H_2O$). Its sweetening power is about one-half that of cane sugar. Specific gravity 1·4. It is dextro-rotatory 54°.

Action of heat.—It suffers no decomposition up to 266° F. (130° C.) At 338° F. (170° C.) water is evolved, and glucosan ($C_6H_{10}O_5$) formed. By the further action of heat, it forms caramel.

It is soluble in water in all proportions. It is not soluble in spirit.

Action of acids.—*Strong sulphuric acid* converts grape sugar into sulpho-saccharic acid. (This acid forms a soluble baric salt.) *Nitric acid* oxidizes it to saccharic or oxalic acid. *Hydrochloric acid* decomposes it. Heated with *organic acids*, it forms conjugate acid compounds, such as tri-aceto-dextrose, $C_6H_9O_3(C_2H_3O_2)_3$. Boiled with *dilute sulphuric or hydrochloric acid*, it forms various brown compounds called ulmin, ulmic acid, etc.

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Solutions of alkalies and alkaline earths decompose it even in the cold, but more rapidly when heated, forming a brown compound (Moor's Test). With yeast, it ferments rapidly and directly at a temperature of 77° F. (25° C.). It unites with certain salts (as NaCl) and metallic oxides (as CaO, BaO, etc.), forming unstable compounds such as $(C_6H_{12}O_6)_2NaCl.OH_2$ and $(C_6H_{12}O_6)_2(BaO)_3,2H_2O$, etc.

It is rapidly oxidized. Hence when boiled in alkaline solutions of silver and copper salts, it quickly reduces them, precipitating metallic silver or the red cuprous oxide. Five molecules of cuprous oxide are exactly reduced by one molecule of grape sugar.

(2.) **Lævulose** (*Lævoglucose; Left-handed Glucose; Mucoid Sugar*) ($C_6H_{12}O_6$).

Natural History.—This sugar occurs, together with glucose, in honey, ripe fruits, etc.

Preparation.—(1.) By heating cane sugar with dilute acids, when a mixture of dextrose and lævulose (*i.e., inverted sugar*) is formed. On neutralizing with lime, calcium compounds of both glucose and lævulose result, the glucose compound being soluble, and the lævulose compound insoluble, in water. The latter after separation is suspended in water, and decomposed by the action of carbonic anhydride or oxalic acid.

(2.) By the action of dilute acids on inulin.

Properties.—A sweet syrup. It may be obtained as an amorphous solid but with difficulty. It is more soluble in water and in spirit than dextrose. It rotates a ray of polarized light to the left. The rotation of glucose to the right is the same at all temperatures, but the extent of rotation to the left in the case of lævulose, varies with the temperature from 53° at 194° F. (90° C.). to 106° at 57·2° F. (14° C.).

Inasmuch as inverted sugar consists of *equal* parts of glucose (= + 56°) and lævulose (= − 106°), it follows that inverted sugar is lævo-rotatory (= − 50°). By heat lævulose forms a body isomeric with glucosan, called lævulosan ($C_6H_{10}O_5$). On oxidation it yields saccharic acid. Its reactions with a ferment and with metallic salts are similar to those of glucose.

(3.) **Galactose** ($C_6H_{12}O_6$) is prepared by boiling milk sugar in dilute acids. It is dextro-rotatory 83 °3′. It ferments easily. It resembles glucose, except that, unlike it and all preceding sugars, it yields mucic acid on oxidation with nitric acid.

(4.) **Sorbite** ($C_6H_{12}O_6$) is prepared from the juice of the berries of the mountain ash. By oxidation with hot nitric acid, it forms oxalic acid. It does not yield alcohol by fermentation with yeast, but it yields lactic and butyric acids with alcohol in contact with cheese and chalk. It is dextro-rotatory 47°.

(5.) **Eucalyn** ($C_6H_{12}O_6$) is a sugar separated when eucalyptus sugar is fermented. It will not ferment, nor is it rendered fermentable by the action of dilute sulphuric acid. It is dextro-rotatory (+ 50°).

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(6.) **Inosite** ($C_6H_{12}O_6$). This is the sugar of muscle. It is also found in kidney beans. It does not undergo alcoholic fermentation, but forms lactic, butyric, and carbonic acids by the action of chalk and cheese. It is without action on a polarized ray.

Glucosides.

There are various bodies found in plants, called glucosides, that are in reality compound ethers of glucose, which yield on decomposition a glucose, together with other substances. The following are the most important of these bodies:—

(1.) **Amygdalin** ($C_{20}H_{27}NO_{11} + 3H_2O$). *Source;* bitter almonds. Under the action of synaptase it forms glucose, bitter almond oil, and hydrocyanic acid. Thus :—

$C_{20}H_{27}NO_{11}$	+	$2H_2O$	=	C_7H_6O	+	HCN	+	$2C_6H_{12}O_6$.
Amygdalin	+	Water	=	Hydride of benzoyl	+	Hydrocyanic acid	+	Glucose.

(2.) **Æsculin** ($C_{21}H_{24}O_{13}$). *Source*; horse-chestnuts.

(3.) **Chitin** ($C_9H_{15}NO_6$). *Source*; wing-cases of insects.

(4.) **Glycyrrhizin** ($C_{24}H_{36}O_9$). *Source*; liquorice sugar.

(5.) **Indican** ($C_{26}H_{31}NO_{17}$). *Source*; indigo.

(6.) **Myronic Acid** ($C_{10}H_{19}NS_2O_{10}$). *Source*; black mustard. By the action of the myrosin (an albuminous ferment) present in the seed, myronic acid forms oil of mustard, glucose, and sulphuric acid.

(7.) **Phlorizin** ($C_{21}H_{24}O_{10},2H_2O$). *Source*; Root bark of apple and cherry-tree.

(8.) **Quercitrin** ($C_{33}H_{30}O_{17}$). *Source*; Quercitron bark.

(9.) **Salicin** ($C_{13}H_{18}O_7$). *Source*; bark of willow, poplar; also found in the castoreum, contained in a gland of the beaver. It forms, under the action of synaptase or emulsin, glucose and saligenin ($C_7H_8O_2$), and by distillation with sulphuric acid and potassic bichromate, salicylol ($C_7H_6O_2$), or the artificial oil of the meadow sweet (Spiræa ulmaria).

(10.) **Populin** ($C_{20}H_{22}O_8$). *Source*; bark of aspen.

(11.) **Ruberythric Acid** ($C_{26}H_{28}O_{14}$). *Source*; madder root.

(12.) **Solanin** ($C_{43}H_{71}NO_{16}$). *Source*; woody nightshade.

(13.) **Tannin** ($C_{27}H_{22}O_{17}$). *Source*; gall-nuts.

GROUP III.—AMYLOSES.

Starches: Fecula-Amidine.

Natural History.—The starches are organised, non-crystalline bodies, found in cells in every part of the vegetable, except in the tip of the bud and in the extremities of the rootlets. Starch is also found in animals, especially in embryonic tissues, as well as in the brain, liver, spleen, and kidneys of adults.

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Preparation.—The tissue is first broken up, and the starch washed out with cold water, in which it is insoluble.

Varieties.—We may recognise four varieties:—

(1.) *Common starch;* (2.) *Lichen starch;* (3.) *Inulin;* (4.) *Paramylon.*

(1.) Common Starch $(C_9H_{10}O_5)_n$.

Preparation.—(*α.*) From *wheat,* which contains 60 per cent. It is extracted either (1) by fermenting the wheat flour for three or four weeks, during which time the gluten putrefies, thereby assisting the separation of the starch (old method); or (2), by simple washing.

(*β.*) From *rice* (83 per cent.), extracted by washing the powdered rice with a weak alkaline lye to dissolve the gluten (Jones patent).

(*γ.*) From *potatoes* (20 per cent.), extracted by rasping and washing.

(*δ.*) From *arrowroot,* Jatropha manihot, etc.

Properties.—A white pulverulent crepitating solid. The form and size of the starch corpuscles vary with its source. It is insoluble in cold water, alcohol or ether. Specific gravity, 1·5.

Action of heat. (*α.*) *On the dry starch.* A moderate heat merely dries the starch corpuscles. A temperature of 320° F. (160° C.) discolors the starch a little, and renders it soluble (dextrin). At higher temperatures it becomes of a buff colour, and evolves water, leaving dextrin. At a still higher temperature, it evolves more water, and leaves caramel. At a still higher temperature, it is decomposed, a carbonaceous residue being left, and carbonic and acetic acids, together with certain empyreumatic oils, evolved.

(*β.*) *Heated with water* to 158° F. (70° C.) the starch corpuscles split, and form with the water a thick paste, called *starch paste.* Boiled for a long time, the solution becomes clear. On the addition of alcohol to the clear solution, it deposits a white precipitate of soluble starch.

Action of acids.—All acids decompose starch; (*α.*) Strong *sulphuric acid* dissolves it, forming a compound acid. Dilute sulphuric acid and heat change it into glucose; (*β.*) *Nitric acid,* when concentrated, forms xyloidin, which is precipitated on the addition of water $(C_{12}H_{19}(NO_2)O_{10})$. A weaker acid converts it into oxalic acid. A very weak acid changes it to dextrin; (*γ.*) *Hydrochloric acid* changes it into glucose. The action of oxalic and tartaric acids (but not of acetic acid) is similar to that of HCl.

Action of alkalies.—These cause starch to form a paste when in solution without heat. Fused with it they form oxalates.

Action of haloids.—Neither chlorine nor bromine have much action on starch in the cold, but when starch is heated in chlorine it is decomposed. The action of iodine is to color the starch blue, the color being destroyed at a little below 212° F. (100° C.), reappearing (if the heat has not been too great) as the solution cools. Ferments, such as yeast and diastase, (like dilute sulphuric acid,) change it into dextrin and glucose.

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(2.) **Lichen Starch** is found in most lichens, such as Iceland and Carageen moss. When boiled with water it forms a jelly. It is converted by acids into glucose. Iodine turns it a greenish brown color. It does not ferment when mixed with yeast or diastase.

(3.) **Inulin Starch** is found in the roots of most of the Compositæ, such as the dahlia, chicory, elecampane, etc. It is an amorphous white substance, decomposed, like starch, by heat. It forms dextrin by long-continued boiling. By the action of dilute acids, it yields lævulose. Iodine has no action upon it.

(4.) **Paramylon,** *glycogen,* or *animal starch,* is found in certain of the lower animals, and also in certain viscera of the higher animals, especially in the placenta. Acids change it into glucose. Iodine has no action upon it.

Uses.—In the *vegetable,* starch acts as a store of nutriment. In the *animal,* its use is a respiratory food. The essential condition for rendering starch useful, either to the vegetable or to the animal, is its conversion into soluble dextrin and sugar.

GUMS ($C_6H_{10}O_5$).

Gums are organic bodies occurring in the juices of plants. They are amorphous, tasteless, and inodorous bodies. They are distinguished from *sugars* by not being susceptible of fermentation, and by forming *mucic acid* when oxidized with nitric acid. From *resins* they may be distinguished by their solubility or by their softening in water, and by their insolubility in alcohol.

Varieties.—*Dextrin, arabin, cerasin, tragacanthin, bassorin, calendulin, saponin, pectin, carrageenin, cydonin.*

(1.) **Dextrin** ($C_6H_{10}O_5$). Dextrin occurs in all vegetable juices, and may be prepared artificially (constituting artificial or British gum), either—

(α.) By heating starch with or without water.

(β.) By heating starch with dilute sulphuric acid.

(γ.) By the action either of diastase, such as is contained in an infusion of malt, or of a similar compound present in the stomach during digestion, on starch.

The properties of dextrine vary somewhat with its source. It dissolves in water, forming a mucilage, from which solution it is precipitated by alcohol and by acetate of lead. Its action on a ray of polarized light is dextro-rotatory (138° 7′).

Iodine colors some specimens of dextrin brown, whilst on others it is without action. By boiling with dilute acids it forms dextrose. It does not ferment with yeast. The pure gum does not reduce an alkaline copper solution.

(2.) **Arabin** ($C_{12}H_{22}O_{11}$) is the principle of gum arabic, and constitutes the soluble portion of other gums. It is soluble in its own weight of water, the solution being unacted upon by iodine. The

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arabin may be precipitated from its aqueous solution by alcohol, by basic acetate of lead, and by potassic silicate.

Arabin is probably *a gummate of lime.* On incineration, arabin yields 3 per cent. of ash, which is almost entirely lime. Gummic acid is said to be soluble in water, like gum, but not to be precipitated from its solution by alcohol, unless an acid or a salt be present. It is lævo-rotatory 36°. By a heat of 212° F. (100° C.) it forms metagummic acid which is insoluble in water.

(3.) **Cerasin** ($C_6H_{10}O_5$) is the insoluble part of cherry-tree, peach, and other such gums. It is said to be a compound of lime and metagummic acid. By long continued boiling it is changed into arabin.

(4.) **Tragacanthin** is the soluble portion of gum tragacanth.

(5.) **Bassorin** is the insoluble portion of gum tragacanth, and forms the chief part of gum bassora. It is soluble both in cold and boiling water.

(6.) **Pectin.** Unripe fleshy fruits contain an insoluble body called *pectose*, to which the hardness of unripe fruits is due. By the action of a ferment present in the fruit, this body forms in the ripe fruit a soluble substance called *pectin.* The peculiarity of pectin is the property it possesses of forming a jelly with acids or alkalies. It is soluble in water, insoluble in alcohol, and without action on a polarized ray.

The solution of *pectin* is neutral. It is precipitated by alcohol, but not by plumbic acetate. By boiling with water it forms *parapectin* which is precipitated by plumbic acetate. By boiling with dilute acid it forms *meta-pectin,* which is acid to litmus, and is precipitated by baric chloride. By the action of bases, all these varieties of pectin are changed into pectic acid.

We are unable to fix definite formulas for these bodies.

REACTIONS TO BE NOTED.

Alcohol (Ethylic alcohol, $C_2H_5(OH)$):—

1. It absorbs moisture. It mixes with water, contraction and heat occurring at the time.

2. Heated in a test tube, (α.) it volatilizes without blackening; (β.) the vapor has a peculiar odor, and (γ.) burns with a blue, smokeless, non-luminous flame.

3. Heated with sulphuric acid, (α.) alcohol does not blacken; (β.) it evolves an ethereal odor. [Methylated spirit turns brown.]

4. Heated with potassic hydrate it gives no action.

Glycerin, $C_3H_5(OH)_3$:—

1. Heated in a test-tube glycerin decomposes without blackening, emitting acrid fumes of acrolein.

2. Its behaviour when heated with sulphuric acid or with potassic hydrate is similar to the action of heat without these reagents.

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3. It has no action on vegetable colors.

4. Nitro-sulphuric acid forms with it the substitution compound nitro-glycerin ($C_3H_5(NO_2)_3O_3$.)

Sugars :—

	Sucrose.	Glucose.
1. Taste	Very sweet	Not very sweet.
2. Action on polarized ray..	Dextro-rotatory 73·8°	Dextro-rotatory 54°.
3. Heated in a test tube ..	Chars; odor of caramel	Chars.
4. Heated with H_2SO_4 ..	Chars rapidly; SO_2 evolved	Chars slowly, forms sulpho-saccharic acid.
5. Heated with potassic hydrate	No change	Becomes dark brown.
6. Heated with potassic cupric tartrate	No red ppt. of Cu_2O	Red precipitate of Cu_2O.
7. Add to the solution two drops of cupric sulphate, and then KHO	Turns blue; on heating little alteration occurs at first; a slight red precipitate falls after a time, but the blue color of the solution remains.	Turns blue; on heating an immediate yellow precipitate occurs, becoming dark red (Cu_2O), the solution rapidly losing its color.

Starch :—

(1.) Under the microscope, starch cells appear as rounded grains, which polarize light.

(2.) Insoluble in cold water. When boiled the cells burst, and the starch forms a paste, shreds of membrane being apparent in the solution.

(3.) It forms a blue compound with free iodine; this compound is, (α.) soluble in pure water, and (β.) insoluble in solutions containing free acid; (γ.) is destroyed by heat, *temporarily* if the heat be slight, but *permanently* if the heat be considerable.

4. It is soluble in strong nitric acid, forming xyloidin.

Gum :—

1. It softens in cold water.
2. Gives no reaction with tincture of iodine.
3. Basic acetate of lead gives with it a white precipitate.

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CHAPTER XXIV.

THE ORGANIC ACIDS.

Relationship to other bodies. MONOBASIC ACIDS: Acetic—Acrylic—Sorbic—Benzoic—Cinnamic—Naphtoic. DIBASIC ACIDS: Succinic—Fumaric—Phthalic. TRIBASIC ACIDS: Tricarballylic—Mesitic. Reactions of the acids.

SUPPLEMENTARY CHAPTER.—Fats and Oils—Soaps—Candles—The Tannins—Ink—Tanning.

ORGANIC ACIDS.

An organic acid may be regarded as an alcohol derivative. It is a compound of a semi-molecule of hydroxyl (OH) with an oxygenated radical.

(1.) *An alcohol* is derived from a hydrocarbon by the substitution of one or more equivalents of the group (OH), for one or more equivalents of H. Thus—

C_2H_6 = *Ethane* and forms $C_2H_5(OH)$ *Ethylic alcohol.*
C_3H_8 = *Propane* ,, ,, $C_3H_7(OH)$ *Propylic alcohol.*

Upon *the number* of equivalents of (OH) substituted for hydrogen atoms, depends the *atomicity* of the alcohol, by which we mean the number of ethers that an alcohol can form by the substitution of a monatomic alcohol radical for the hydrogen of the group (OH); Thus—

Monatomic alcohol	Diatomic alcohol	Triatomic alcohol.
$C_3H_7(OH)$	$C_3H_6(OH)_2$	$C_3H_5(OH)_3$.
Propyl alcohol;	*Propene alcohol;*	*Propenyl alcohol.*

(2.) *An organic acid* is derived from an alcohol by the equivalent substitution of O″ for H_2, or of O_2 for H_4, etc. Thus—

$C_2H_5(OH)$ *Ethylic alcohol* forms $C_2H_3O(OH)$ *Acetic acid;*
$C_3H_7(OH)$ *Propylic alcohol* ,, $C_3H_5O(OH)$ *Propylic acid.*

(3.) An alcohol may yield more than one acid. The number of acids an alcohol is capable of forming may be determined by the number of times that the group (CH_2.OH) enters into the molecule of the alcohol. Thus—

Ethylic alcohol $C_2H_5(OH)$ contains but *one* of the group CH_2OH ($+CH_3$). It therefore forms only *one* acid.

Ethene alcohol $C_2H_4(OH)_2$ contains *two* of the group CH_2OH. It therefore forms *two* acids.

(4.) But inasmuch as the change of an alcohol into an acid, consists in the substitution of O for H_2, or in other words in the conversion of the group CH_2OH of the alcohol, into COOH in the acid (which latter

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group is termed *carboxyl*), it follows that the number of equivalents of carboxyl in the acid, determines the basicity of the acid; in other words, that the number of groups of carboxyl indicates the number of hydrogen atoms in the acid that may be replaced by metals to form salts. Thus, $C_2H_4O_2$ is *acetic acid*. It contains only *one* of the group COOH; it therefore is a *monobasic* acid, *i. e.*, only one atom of its hydrogen can be replaced by a metal in the formation of salts.

$C_2H_2O_4$ is *oxalic acid*. It contains *two* of the group COOH; it therefore is *dibasic*, *i.e.*, the molecule may have two atoms of its hydrogen replaced, either by two of a monad metal, or by one dyad metal, in the formation of salts.

(5.) It is evident, therefore, that the basicity of any acid, corresponds with the basicity of the alcohol from which the acid was derived. Many of the acids known have been actually derived from alcohols, whilst many, as yet, have not been classified.

Constitution of the Acids.—Acids have been regarded as formed on the type of a molecule of water, by the substitution of an acid or oxygenated radical for *one* of the hydrogens (if the radical be univalent) of the water molecule, just as alcohols are regarded as formed on the type of a molecule of water by the substitution of an alcohol or hydrocarbon radical for *one* of hydrogen. If the radicals be divalent, the acids and alcohols are then regarded as formed on the double water type, etc. Thus—

(α.) $\left.\begin{matrix}H\\H\end{matrix}\right\}O$ = Water (*single mol.*); $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$ = Ethylic alcohol; $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$ = Acetic acid.

(β.) $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$ = Water (*double mol.*); $\left.\begin{matrix}(C_3H_6)''\\H_2\end{matrix}\right\}O_2$ = Propene glycol; $\left.\begin{matrix}(C_3H_4O)''\\H_2\end{matrix}\right\}O_2$ = Lactic acid.

The acid radicals are denoted by names ending in *yl*, as *acetyl*, the radical of acetic acid, etc.

Acid Derivatives.

(1.) **Salts.**—Organic acids (as we have said) are of different basicities, according to the number of times that the group CO.OH occurs in the molecule. When the acid is acted upon by a metallic carbonate, hydrate or oxide, the H of this group (carboxyl) is exchanged for a metal to form a salt.

(α.) *Monobasic acids*, such as acetic acid, $CH_3CO(OH)$, forms (1) *normal salts*, as sodic acetate, $CH_3CO(ONa)$; (2) *acid salts*, formed by the combination of a normal salt with a molecule of the acid, as acid potassic acetate, $(C_2H_3O)_2(OK)(OH)$; and (3) *basic salts*, formed by the combination of a normal salt with one or more molecules of a metallic oxide or hydrate, as triplumbic acetate, $Pb''(C_2H_3O_2)_2,2PbO$, etc.

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(β.) *Dibasic acids*, such as oxalic acid, $C_2O_2(OH)_2$, form (1) *normal salts*, as ammonic oxalate, $C_2O_2(ONH_4)_2$, where all the displaceable hydrogen is replaced by a metal; and (2) *acid salts*, as acid ammonic oxalate, $C_2O_2(OH)(ONH_4)$, where one-half of the displaceable hydrogen is replaced by a metal.

(2.) Acid Anhydrides or Oxides.—These are bodies formed by the substitution of the hydrogen of the carboxyl in the acid, by an acid radical. Thus, $CH_3CO(OH)$ being acetic acid,—

(α.) $[CH_3CO(CH_3CO)O]$ = acetic oxide or anhydride.

(β.) $[CH_3CO(C_7H_5O)O]$ = acetobenzoic oxide.

Thus the acid radical may be the same as that already present in the body, as in (α), or it may be different, as in (β). Various mixed anhydrides may in this way be formed.

Preparation.—(1.) By the action of the acid chlorides either on the acids or on their salts.

(2.) By the action of acid chlorides on metallic oxides.

Properties.—(1.) By the action of *water*, the anhydrides become acids; (2) with *phosphoric chloride* (PCl_5), they form acid chlorides; (3) by the action of *alcohols*, they form ethereal salts; (4) with *ammonia*, they form acid amides.

(3.) Acid Peroxides.—These bodies bear the same relationship to acid oxides, that PbO bears to PbO_2. Thus:—

$(CH_3CO)_2O$ = *acetic oxide*; $(CH_3CO)_2O_2$ = *acetic peroxide*.

Preparation.—By the action of a metallic peroxide (as BaO_2) on an acid anhydride or chloride.

Properties.—The acid peroxides are powerful oxidising agents.

(4.) Compound Ethers.—*Ethereal salts.* Bodies formed by the substitution of the replaceable hydrogen of an acid, by an alcohol (hydrocarbon) radical. Thus:—

Acetic acid, $CH_3CO(OH)$, forms $CH_3CO(OC_2H_5)$, *ethylic acetate*.

A similar formation takes place in the case of the mineral acids. Thus:—

Sulphuric acid, H_2SO_4, forms $(C_2H_5)_2SO_4$, *ethylic sulphate*.

Further, as we have normal and acid metallic salts, so we may also have normal and acid ethereal salts.

Preparation.—(1.) By the action of alcohols, either on the acids, the acid chlorides, or the anhydrides.

(2.) By the action of the acid ethereal salts of sulphuric acid on the alkaline salts of the acids.

Properties.—Stable bodies. When heated with water they form the acid and the alcohol from which they were derived.

(5.) Acid Chlorides, Bromides, and Iodides. These are bodies formed by the substitution of the (OH) in the carboxyl group of the acid, by either chlorine, bromine, or iodine. Thus—

Acetic acid, $CH_3CO(OH)$, forms $CH_3CO(Cl)$, *acetyl chloride*.

Succinic acid, $C_2H_4C_2O_2(OH)_2$, forms $C_2H_4C_2O_2(Cl_2)$, *succinyl chloride*.

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Preparation.—By the action of the haloid phosphorus compounds on the acids, or on their metallic salts.

Properties.—Decomposed by water into the organic and haloid acids. Thus :—

$CH_3CO(Cl)$	+	H_2O	=	$CH_3CO(OH)$	+	HCl.
Acetyl chloride	+	Water	=	Acetic acid	+	Hydrochloric acid.

(6.) Acid Amides (*Amidated acids*).—Bodies formed by the substitution of the (OH) in the carboxyl group of the acid by amidogen (NH_2). The monobasic acids yield normal amides only, whilst the dibasic acids yield both normal and acid amides. Thus :—

Acetic acid $CH_3CO(OH)$, forms $CH_3CO(NH_2)$ *Acetamide* (neutral).
Succinic acid $C_2H_4C_2O_2(OH)_2$, forms $C_2H_4C_2O_2(NH_2)(OH)$ *Succinamide* (acid).
,, ,, ,, $C_2H_4C_2O_2(NH_2)_2$ *Succinamide* (neutral).

Preparation.—(1.) By the action of heat on the ammonic salts of the acids, whereby water is abstracted. Thus :—

$CH_3CO(ONH_4)$	=	$CH_3CO(NH_2)$	+	H_2O.	
Ammonic acetate	=	Acetamide	+	Water.	

(2.) By the action of ammonia either (α) on the compound ethers or (β) on the acid chlorides.

(α.)	$CH_3CO(OC_2H_5)$	+	NH_3	=	$C_2H_5(OH)$	+	$CH_3CO(NH_2)$.	
	Ethylic acetate	+	Ammonia	=	Ethylic alcohol	+	Acetamide.	
(β.)	$CH_3CO(Cl)$	+	$2NH_3$	=	NH_4Cl	+	$CH_3CO(NH_2)$.	
	Acetyl chloride	+	Ammonia	=	Ammonic chloride	+	Acetamide.	

Properties.—When the acid amides are heated with water, the ammoniacal salts are re-formed. When distilled with phosphoric anhydride, they become "nitriles" or alcoholic cyanides. Thus:—

$CH_3CO(NH_2)$	+	P_2O_5	=	CH_3CN(or$(C_2H_3)'''N$)	+	$2HPO_3$.	
Acetamide	+	Phosphoric anhydride	=	Methyl cyanide (*or* ethenyl nitrile)	+	Phosphoric acid.	

(7.) Haloid salts of the acids. These are compounds formed from the metallic salts, by the substitution of the metal by *chlorine*, etc. Thus :—

Potassic acetate $CH_3CO(OK)$, forms $CH_3CO(OCl)$ *chlorine acetate.*

Properties.—Very unstable bodies. They explode at a low temperature.

(8.) Substitution Derivatives.—By the direct action of the haloid elements on the acids, the substitution of one or more chlorine atoms for hydrogen may be effected. Thus :—

$CH_3CO(OH)$ = Acetic acid.

$CH_2ClCO(OH)$ Monochloracetic acid.	$CH_2BrCO(OH)$ Monobromacetic acid.
$CHCl_2CO(OH)$ Dichloracetic acid.	$CHBr_2CO(OH)$ Dibromacetic acid.
$CCl_3CO(OH)$ Trichloracetic acid.	

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These substitution acids form salts, compound ethers, acid chlorides, etc., like the original acid.

The organic acids are divided into three great classes according to the number of carboxyl groups (CO.OH) which they contain, or in other words, according to their basicity :—

I. Monobasic acids; II. Dibasic acids; III. Tribasic acids.

These may be further subdivided as follows :—

(A.) Monobasic Acids.

	SERIES.	Hydrocarbon from which derived.	Formula.	Example.
I.	Acetic series .. (fatty acids)	C_nH_{2n+2}	$C_nH_{2n+1}CO(OH)$	Acetic acid $CH_3CO(OH)$
	(α.) Lactic series ..		$C_nH_{2n}(OH).CO(OH)$	Lactic acid $C_2H_4(OH)CO(OH)$
	(β.) Pyruvic series		$C\ H_{2n-1}OCO(OH)$	Pyruvic acid $C_2H_3OCO(OH)$
	(γ.) Glyoxylic series		$C_nH_{2n-1}(OH)_2.CO(OH)$	Glyceric acid $CH_2(OH)CH(OH)CO(OH)$
II.	Acrylic series ..	C_nH_{2n}	$C_nH_{2n-1}CO(OH)$	Acrylic acid $C_2H_3CO(OH)$
II.	Sorbic series ..	C_nH_{2n-2}	$C_nH_{2n-3}CO(OH)$	Sorbic acid $C_5H_7CO(OH)$
IV.	Benzoic series ..	C_nH_{2n-6}	$C_nH_{2n-7}CO(OH)$	Benzoic acid $C_6H_5CO(OH)$
	(α.) Oxybenzoic series		$C_nH_{2n-8}(OH)CO(OH)$	Salicylic acid $C_6H_4(OH)CO(OH)$
	(β.) Dioxybenzoic series		$C_nH_{2n-9}(OH)_2CO(OH)$	Oxysalicylic acid $C_6H_3(OH)_2CO(OH)$
V.	(γ.) Gallic series..		$C_nH_{2n-10}(OH)_3CO(OH)$	Gallic acid $C_6H_2(OH)_3CO(OH)$
	Cinnamic series ..	C_nH_{2n-8}	$C_nH_{2n-9}CO(OH)$	Cinnamic acid $C_8H_7CO(OH)$
	(α.) $C_nH_{2n-11}CO(OH)$		$C_nH_{2n-11}CO(OH)$	Phenyl propiolic acid $C_6H_5C_2CO(OH)$
VI.	Naphtoic series ..	C_nH_{2n-12}	$C_nH_{2n-13}CO(OH)$	Naphtoic acid $C_{10}H_7CO(OH)$
	(α.) $C_nH_{2n-19}CO(OH)$..		$C_nH_{2n-19}CO(OH)$	Anthracene-carboxylic acid $C_{14}H_9CO(OH)$

(B.) Dibasic Acids.

	SERIES.	Hydrocarbon from which derived.	Formula.	Example.
I.	Succinic series ..	C_nH_{2n+2}	$C_nH_{2n}(COOH)_2$	Succinic acid $C_2H_4(COOH)_2$
	(α.) Malic series ..		$C_nH_{2n-1}(OH)(COOH)_2$	Malic acid $C_2H_3(OH)(COOH)_2$
	(β.) Tartaric series		$C_nH_{2n-2}(OH)_2(COOH)_2$	Tartaric acid $C_2H_2(OH)_2(COOH)_2$
II.	Fumaric series ..	C_nH_{2n}	$C_nH_{2n-2}(COOH)_2$	Fumaric acid $C_2H_2(COOH)_2$
II.	Phthalic series ..	C_nH_{2n-6}	$C_nH_{2n-8}(COOH)_2$	Phthalic acid $C_6H_4(COOH)_2$

(C.) Tribasic Acids.

	SERIES.	Hydrocarbon from which derived.	Formula of Acids.	Example.
I.	Tricarballylic series	C_nH_{2n+2}	$C_nH_{2n-1}(COOH)_3$	Tricarballylic acid $C_3H_5(COOH)_3$
II.	Mesitic series ..	C_nH_{2n-6}	$C_nH_{2n-9}(COOH)_3$	Mesitic acid $C_6H_3(COOH)_3$

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A. MONOBASIC ACIDS.

Acetic Series.

SERIES I. *Formula* $(C_nH_{2n+1}.CO(OH))$.

Of these we recognize three groups—

(*a.*) *Normal or primary acids* $\begin{cases} C(C_nH_{2n+1})H_2 \\ CO(OH) \end{cases}$;

derivatives of primary alcohols (*see* page 559), *i.e.*, an alcohol where one hydrogen atom of carbinol $CH_3(OH)$ has been replaced by a radical of the formula C_nH_{2n+1}

(*β.*) *Secondary acids* $\begin{cases} C(C_nH_{2n+1})_2H \\ CO(OH) \end{cases}$;

derivatives of secondary alcohols, *i.e.*, an alcohol where two hydrogen atoms of carbinol $CH_3(OH)$ have been replaced by two radicals of the formula C_nH_{2n+1}.

(*γ.*) *Tertiary acids* $\begin{cases} C(C_nH_{2n+1})_3 \\ CO(OH) \end{cases}$;

derivatives of tertiary alcohols, *i.e.*, an alcohol where three hydrogen atoms of carbinol $CH_3(OH)$ have been replaced by three radicals of the formula C_nH_{2n+1}. Thus—

From the *alcohols* we obtain the *acids*:—

Alcohols.	Acids.	Example.
(*a.*) $C(C_nH_{2n+1})H_2(OH)$ Primary alcohol.	$\begin{cases} C(C_nH_{2n-1})H_2 \\ COOH \end{cases}$; Primary acid.	$\begin{cases} C(CH_3)H_2 \\ COOH \end{cases}$ Propionic or methacetic acid.
(*β.*) $C(C_nH_{2n+1})_2H(OH)$ Secondary alcohol.	$\begin{cases} C(C_nH_{2n+1})_2H \\ COOH \end{cases}$; Secondary acid.	$\begin{cases} C(CH_3)_2H \\ COOH \end{cases}$ Isobutyric or dimethacetic acid.
(*γ.*) $C(C_nH_{2n+1})_3(OH)$ Tertiary alcohol.	$\begin{cases} C(C_nH_{2n+1})_3 \\ COOH \end{cases}$; Tertiary acid.	$\begin{cases} C(CH_3)_3 \\ COOH \end{cases}$ Trimethacetic acid.

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(a.) *Normal acids of the acetic series* $\left\{\begin{matrix} C(C_nH_{2n+1})H_2 \\ CO(OH) \end{matrix}\right.$

ACIDS.	Formula.	Fusing Pt.		Boiling Pt.		Sp. Gr.	Molecular Weight.	Remarks.
		° F.	° C.	° F.	° C.	° C.		
Formic acid.. .. (Methylic acid)	HCO(OH)*	33·8	1	212·0	100	1·23 at 16	30	See page 599.
Acetic acid .. .. (Ethylic acid)	$CH_3CO(OH)$†	62·6	17	242·6	117	1·002 at 20	60	See page 600.
Propionic acid .. (Propylic acid)	$C_2H_5CO(OH)$	below		285·8	141	·996 at 19	74	See page 602.
Butyric acid.. .. (Tetrylic acid)	$C_3H_7CO(OH)$	—4	—20	321·8	161	·981 at 0	88	See page 602.
Valeric acid.. .. (Pentylic acid)	$C_4H_9CO(OH)$			347·0	175	·957 at 0	102	See page 603.
Caproic acid.. . (Hexylic acid)	$C_5H_{11}CO(OH)$	41·0	5·0	388·4	198	·943 at 0	116	See page 603.
Œnanthylic acid.. (Heptylic acid)	$C_6H_{13}CO(OH)$			413·6	212	·934 at 0	130	See page 604.
Caprylic acid .. (Octylic acid)	$C_7H_{15}CO(OH)$	57·2	14·0	456·8	236		144	Occurs as a glyceride in the butter of cows' milk and in cocoa nut oil.
Pelargonic acid .. (Nonylic acid)	$C_8H_{17}CO(OH)$	64·4	18	500·0	260	·9065 at 17	158	Occurs in the leaves of the geranium, and may be prepared by the action of nitric acid on oil of rue.
Capric acid .. .. (Rutic acid)	$C_9H_{19}CO(OH)$	86·0	30				172	Occurs as a glyceride in butter, and also in cocoa nut oil, and in fusel oil. May be prepared by the oxidation of oleic acid.
Lauric acid	$C_{10}H_{21}CO(OH)$	110·4	43·6				200	Occurs as a glyceride in the fats of the bay tree, pichurim beans, cocoa nut oil, spermaceti, etc.
Myristic acid ..	$C_{13}H_{27}CO(OH)$	128·8	53·8				228	Occurs as a glyceride in nutmeg butter, cocoa nut oil, spermaceti, and otaba fat.
Palmitic acid ..	$C_{15}H_{31}CO(OH)$	143·6	62·0				256	See page 604.
Margaric acid ..	$C_{16}H_{33}CO(OH)$	140·0	60·0				258	See page 604.
Stearic acid.. ..	$C_{17}H_{35}CO(OH)$	156·5	69·2			1·01 at 0	284	See page 604.
Arachidic acid ..	$C_{19}H_{39}CO(OH)$	167·0	75·1				312	A white crystalline fat, prepared by the saponification of the oil of the earth-nut (arachis hypogæa).
Behenic acid ..	$C_{21}H_{43}CO(OH)$	168·8	76·0				340	A white crystalline fat, prepared by the saponification of oil of ben.
Hyænasic acid ..	$C_{24}H_{49}CO(OH)$	170·6	77·0					
Cerotic acid.. ..	$C_{26}H_{53}CO(OH)$	172·4	78·0				410	Prepared from cerin (viz., that portion of bees' wax soluble in boiling alcohol), or from Chinese wax, a fat produced on certain trees in China by the puncture of a species of coccus.
Melissic acid ..	$C_{29}H_{59}CO(OH)$	190·4	88·0				452	Prepared by heating melissic alcohol with potassic hydrate.

* The radical $C(C_nH_{2n+1})H_2$ in formic acid is replaced by H.
† The value of the $_n$ in the general formula for acetic acid = 0.

Natural History (*General*).—Many of these acids are met with in nature *in a free state*; *e.g.*, Formic acid is found in ants and in nettles, valeric acid in valerian root, etc. Certain of them occur naturally as *ethereal salts*, such as, *e.g.*, cetylic palmitate in spermaceti, glyceric stearate in beef and mutton fat, and glyceric palmitate in palm oil, etc. (Hence the reason that these acids are called the fatty series of acids). The first nine terms of the series have been prepared artificially.

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Preparation (General) :—

(1.) From *the corresponding primary alcohols.* By simple oxidation by such means as exposure to air on platinum black, or by heating with a solution of chromic acid, etc.,

$CH_3.CH_2OH$	+	O_2	=	$CH_3.CO(OH)$	+	H_2O.
Ethylic alcohol	+	Oxygen	=	Acetic acid	+	Water.

(2.) From *the corresponding aldehydes.* By oxidation.

$CH_3.COH$	+	O	=	$CH_3.CO(OH)$.
Acetic aldehyde	+	Oxygen	=	Acetic acid.

(3.) *From the cyanides of the hydrocarbons* C_nH_{2n+1}. By the action either of acids or of alkalies.

(α.) $C_nH_{2n+1},CN + 2H_2O + HCl = C_nH_{2n+1},CO(OH) + NH_4Cl$.

(β.) $C_nH_{2n+1},CN + H_2O + KHO = C_nH_{2n+1},CO(OK) + NH_3$.

[The cyanides are formed by the action of potassic cyanide on a haloid derivative of a hydrocarbon, and in some cases by distilling potassic cyanide with the potassic salts of the sulphonic acids.]

(4.) By the action of carbonic anhydride on a compound of the alcohol radicals of the methyl series with potassium or sodium. Thus :—

CH_3Na	+	CO_2	=	$CH_3.CO(ONa)$.
Sodic methide	+	Carbonic anhydride	=	Sodic acetate.

(5.) By the action of water on the corresponding acid chlorides. Thus —

C_2H_3OCl	+	H_2O	=	HCl	+	$CH_3.CO(OH)$.
Acetyl chloride	+	Water	=	Hydrochloric acid	+	Acetic acid.

General Reactions of the Acids of the Acetic Series.

1. When these acids are submitted to electrolysis, the nascent oxygen evolved from the positive pole sets free the radical and resolves the carboxyl into water and carbonic anhydride ($2(CH_3.CO.OH) + O = (CH_3)_2 + 2CO_2 + H_2O$).

2. When the ammonic salt of these acids is heated with phosphoric anhydride, the salt parts with its water, and forms a nitrile or abnormal cyanide of the radical next below it. Thus:—

$CH_3.CO(ONH_4)$	+	$2P_2O_5$	=	$CH_3(CN)'''$	+	$4HPO_3$.
Ammonic acetate	+	Phosphoric anhydride	=	Methylic nitrile	+	Metaphosphoric acid.

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3. By distilling the potassic salt of an acid of the acetic series with an equivalent quantity of potassic formate, the acid is converted into the aldehyde. Thus:—

$$\underset{\text{Potassic acetate}}{CH_3CO(OK)} + \underset{\text{Potassic formate}}{HCO(OK)} = \underset{\text{Acetic aldehyde}}{CH_3COH} + \underset{\text{Potassic carbonate.}}{K_2CO_3}.$$

When this aldehyde is treated with nascent hydrogen it is converted into a primary alcohol.

4. By the distillation of the dry baric or calcic salt of an acid, a ketone is formed. Thus:—

$$\underset{\text{Calcic acetate}}{Ca(C_2H_3O_2)_2} = \underset{\text{Acetone}}{CO(CH_3)_2} + \underset{\text{Calcic carbonate.}}{Ca''CO_3}.$$

When the ketone is treated with nascent hydrogen it is converted into a secondary alcohol.

5. By heating the acids and the alcohols together in sealed tubes, the compound ethers are formed (*see* page 593).

We now proceed to examine the acids in detail.

Formic Acid ($HCO(OH)=CH_2O_2$). [*Molecular weight*, 46. *Specific gravity of liquid*, 1·23. *Fuses at* 33·8° F. (1° C.), *and boils at* 212° F. (100° C.)

Synonyms.—Methylic acid; Hydric formate.

Natural History.—It constitutes the active principle of the stinging matter of ants, nettles, etc.

Preparation.—(1.) By the oxidation of methylic alcohol.

$$\underset{\text{Methylic alcohol}}{CH_3(OH)} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Formic acid}}{HCO(OH)} + \underset{\text{Water.}}{H_2O}$$

(2.) By the oxidation of numerous organic bodies, such as gum, sugar, starch, etc.

(3.) By the action of heat on oxalic acid. (The acid should in the first place be mixed with sand or glycerine.)

$$\underset{\text{Oxalic acid}}{C_2H_2O_4} = \underset{\text{Formic acid}}{HCO(OH)} + \underset{\text{Carbonic anhydride.}}{CO_2}.$$

(4.) By the action of water vapor and carbonic anhydride on potassium, the potassic salt of formic acid is produced.

$$\underset{\text{Potassium}}{K_2} + \underset{\text{Carbonic anhydride}}{2CO_2} + \underset{\text{Water}}{H_2O} = \underset{\text{Potassic formate}}{HCO(KO)} + \underset{\text{Hydric potassic carbonate.}}{KHCO_3}.$$

(5.) When silent electrical discharges are passed through a mixture of hydrogen and carbonic anhydride, traces of formic acid are said to be produced. (Brodie.)

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(5.) By the action of potassic hydrate (α) on *chloroform*, (β) on *carbonic oxide*, and (γ) on *hydrocyanic acid*.

(α.) $CHCl_3 + 4KHO = HCO(KO) + 3KCl + 2H_2O$.
Chloroform + Potassic hydrate = Potassic formate + Potassic chloride + Water.

(β.) $CO + KHO = HCO(OK)$.
Carbonic oxide + Potassic hydrate = Potassic formate.

(γ.) $HCN + KHO + H_2O = HCO(OK) + NH_3$.
Hydrocyanic acid + Potassic hydrate + Water = Potassic formate + Ammonia.

Properties.—(α.) *Physical.* A colorless, inflammable, corrosive liquid, burning with a blue flame. The vapor has a very penetrating odor. Sp. Gr. 1·23. When cooled to below 32° F. (0° C.) it forms brilliant tabular crystals. It boils at 212° F. (100° C.). It dissolves in water freely, the solution having a very acid reaction. It decomposes carbonates readily. By the action of alcohol it may be partially converted into ethyl formate.

(β.) *Chemical.* With *sulphuric acid*, formic acid breaks up into water and carbonic oxide; with *strong bases* it forms oxalic acid, hydrogen being evolved ($2HCO(OH) + BaO = C_2O_2(BaO_2) + H_2 + H_2O$). With *chlorine*, it forms hydrochloric acid and carbonic anhydride ($HCO(OH) + Cl_2 = 2HCl + CO_2$).

It is a powerful reducing agent. Thus it converts mercuric chloride into mercurous chloride (calomel), and reduces metallic mercury when mixed with mercuric oxide ($HCO(OH) + HgO = CO_2 + Hg + H_2O$). This reducing action of formic acid on metallic salts, distinguishes it from all other acids of this group.

It forms salts called formates, all of which are soluble, and may be expressed by the formulæ $HCO(OM')$; $2HCO(O_2M'')$; $3HCO(O_3M''')$.

Acetic Acid ($C_2H_4O_2 = CH_3CO(OH)$). [*Molecular weight*, 60. *Specific gravity*, 1·063. *Fuses at* 62·6° F. (17° C.), *and boils at* 246·2° F. (119° C.).

Synonyms.—*Ethylic acid; Hydric acetate; Spirits of vinegar.*

Natural History.—It occurs in small quantities in animal fluids, and also in the juices of plants.

Preparation.—By the general processes already described (page 598).

(2.) It is also produced during the destructive distillation of wood (*see* page 497); and

(3.) During the (so-called) acetous fermentation (*see* page 485).

Glacial acetic acid ($C_2H_4O_2$) is prepared by distilling sodic acetate with concentrated sulphuric acid.

Properties.—Acetic acid is a colorless, pungent, corrosive liquid,

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solidifying to a white crystalline mass at 62·6° F. (17° C.), and boiling at 246·2° F. (119° C.). Sp. Gr. 1·063. The vapor is inflammable.

Its vapor density exhibits an anomalous behaviour. Thus, at a very high temperature, its vapor has a normal density of 30 (Mol. Wt. 60), whilst at a few degrees above its boiling point, the vapor has the abnormal density of 45. This is explained by supposing that at the lower temperature the vapor is not a true gas, but commences, so to speak, to behave, at this low temperature, as a liquid.

It mixes with alcohol, ether, and water, in all proportions. On the addition of water its specific gravity rises, until the proportions correspond to a hydrate of the formula C_2H_4O,H_2O. By adding more water the specific gravity sinks. The acid dissolves camphor, etc. When potassic acetate is distilled with arsenious oxide, it yields kakodyl.

Metallic Salts of Acetic Acid.

Of these the following are the most important :—

	Formula.	Remarks.
Potassic acetate, normal ..	$KC_2H_3O_2$	A deliquescent salt, soluble in water and alcohol.
,, acid ..	$KC_2H_3O_2,C_2H_4O_2$	Decomposes at 392° F. (200° C.), giving off the glacial acid.
Sodic acetate	$NaC_2H_3O_2,3H_2O$	Melts at 550·4° F. (288° C.); decomposes at 599° F. (315° C.).
Ammonic acetate, neutral..	$NH_4C_2H_3O_2$	Spiritus Mindereri is the aqueous solution of the B.P.
,, acid ..	$NH_4C_2H_3O_2,C_2H_4O_2$	
Plumbic acetate, normal .. (Sugar of lead)	$Pb''(C_2H_3O_2)_2 3H_2O$	Prepared by dissolving litharge in acetic acid.
,, basic	$2Pb''(C_2H_3O_2)_2.PbO$	The solution constitutes goulard water.
	$Pb''(C_2H_3O_2)_2 2PbO$	
Cupric acetate, normal ..	$Cu''(C_2H_3O_2)_2+aq$	
,, basic	$2Cu''(C_2H_3O_2)_2CuO,6H_2O$	
	$Cu''(C_2H_3O_2)_2,2CuO,3H_2O$	
Argentic acetate..	$Ag(C_2H_3O_2)$	
Aluminic acetate, neutral ..	$(Al_2)^{vi}(C_2H_3O_2)_6$	Much used in calico printing, the acetic acid being capable of being driven off at a low temperature.
,, basic ..	$Al_2O_3,2C_4H_6O_3,4H_2O$	
Ferrous acetate	$Fe''(C_2H_3O_2)_2$	
Ferric acetate	$(Fe_2)^{vi}(C_2H_3O_2)_6$	
Zincic acetate	$Zn''(C_2H_3O_2)_2 2H_2O$	

The further important derivatives of acetic acid are stated in the following table :—

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Derivatives of Acetic Acid.

Names.	Formula.	Sp. Gr.	Boiling Pt.		Remarks.
			° F.	° C.	
Methylic acetate	$CH_3CO(OCH_3)$	0·9562	131·9	55·5	Soluble in alcohol, water, and ether.
Ethylic acetate .. .. (Acetic ether).	$CH_3CO(OC_2H_5)$	0·890	170·6	77·0	With ammonia it yields *acetamide*. Hydrogen is said to be evolved when ethylic acetate is heated with sodium.
Amylic acetate	$CH_3CO(OC_5H_{11})$		300·2	149·0	Odor of Jargonelle pear.
Acetic chloride .. .. (Acetyl chloride).	CH_3COCl		131·0	55·0	A colorless liquid, decomposed by water. Prepared by the action of PCl_5 on glacial acetic acid.
Acetic anhydride	$\left.\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\right\}O$		280·4	138·0	A heavy oil; prepared by the action of acetyl chloride on potassic acetate.
Acetic peroxide	$\left.\begin{matrix}CH_3COO\\CH_3COO\end{matrix}\right\}$				Prepared by the action of BaO_2 on acetic anhydride.
Monochloracetic acid ..	$CH_2Cl.COOH$		366·8	186·0	Prepared by the action of chlorine on glacial acetic acid in sunlight. A solid body, melting at 147·2° F. (61° C.).
Dichloracetic acid	$CHCl_2COOH$	1·5216	221·0	105·0	Prepared by exposing monochloracetic acid to the action of dry chlorine. A liquid.
Trichloracetic acid ..	$CCl_3.COOH$	1·617 of fused acid.	390·2	199·0	Prepared by exposing a little of the crystallized acid in a bottle of chlorine to sunlight for several hours. A solid body, melting at 114·8° F. (46° C.).
Monobromacetic acid ..	$CH_2BrCOOH$				These acids are prepared by heating bromine with glacial acetic acid in sealed tubes.
Dibromacetic acid	$CHBr_2COOH$				
Tribromacetic acid ..	CBr_3COOH				
Thiacetic acid	$CH_3CO(SH)$		203·0	95·0	Prepared by distilling together acetic acid and P_2S_5. A colorless liquid.
Iodacetic acid..	$CH_2ICO(OH)$				
Acetamide	$CH_3CO(NH_2)$		429·8	221·0	A solid, melting at 172·4° F. (78° C.). Prepared by the distillation of ammonic acetate. It combines with acids, and yields metallic derivatives.
Amidoacetic acid.. .. (Glycocine, Glycocol).	$CH_2(NH_2)CO(OH)$				A solid, formed by the action of ammonia on brom-acetic acid.
Methyl glycocine . .. (Sarcosine).	$C_3H_7NO_2$				Prepared either by digesting ethyl chloracetate with an excess of a concentrated solution of methylamine, or by boiling kreatine with baryta water.

Propionic Acid ($C_3H_6O_2=C_2H_5COOH$). [*Molecular weight*, 74. *Boils at* 284° F. (140° C.).]

Synonyms.—Methacetic acid; Propylic acid.

Preparation.—(1.) By the general methods already described (page 598).

(2.) By the action of hydriodic acid on lactic acid.

(3.) By the fermentation either of glycerine or of sugar with putrid cheese, in the presence of calcic carbonate.

Properties.—A crystalline solid, boiling at 284° F. (140° C.). It is soluble in water. It forms salts called propionates.

Butyric Acid ($C_4H_8O_2 = C_3H_7CO(OH)$). [*Molecular weight*, 88. *Specific gravity of liquid*, 0·9886. *Fuses below* − 4° F. (− 20° C.) *Boils at* 321·8° F. (161° C.).]

Synonyms.—Ethacetic acid; Diethacetic acid; Tetrylic acid.

Natural History.—It is found in butter, in tamarinds, in various animal secretions, and in various kinds of decomposing animal and vegetable matters.

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Varieties.—The acid is known in two isomeric conditions; viz., as *normal butyric acid* ($CH_3.CH_2.CH_2.CO(OH)$), and as *isobutyric acid* $CH(CH_3)_2CO(OH)$. They are both colorless liquids, and both, when heated, yield acetic acid and carbonic anhydride.

Preparation of (α) *normal butyric acid.*—(1.) By the oxidation of normal butylic alcohol ($CH_2.CH_2.CH_3.CH_2.OH$).

(2.) By the fermentation of sugar with cheese and chalk (*see* page 485).

Properties.—At 32° F. (0° C.) it has a Sp. Gr. of 0·981. It boils at 323·6° to 325·4° F. (162° to 163° C.).

Preparation of (α) *isobutyric acid.*—By the oxidation of isobutylic alcohol ($CH(CH_3)_2CH_2OH$).

Properties.—At 0° C. it has a Sp. Gr. of 0·959. It boils at 309·2° F. (154° C.). It is more easily decomposed by heat than the normal acid.

Valeric Acid, $C_5H_{10}O_2=C_4H_9.CO(OH)$. *Molecular Weight,* 102. *Sp. Gr. of liquid,* 0·937. *Boils at* 347° F. (175° C.).

Synonyms.—Valerianic acid; Pentylic acid.

Natural History.—It is found in valerian root, in the berries of the guelder rose, and in many other plants.

Varieties.—It exists in four isomeric states, *viz.*—

(α.) *Normal valeric* or *valerianic acid* (propylacetic acid)—

$CH_3.CH_2.CH_2.CH_2.CO(OH)$.

Preparation.—By the oxidation of normal amylic alcohol.

Properties.—An oily liquid, having an acid taste, burning with a smoky flame, and boiling at 365° F. (185° C.). It has a specific gravity of 0·9577 at 32° F. (0° C.).

(β.) *Iso-valeric acid* (iso-propylacetic acid) $CH(CH_3)_2.CH_2.CO(OH)$.

Preparation.—By the oxidation of iso-amylic alcohol.

Properties.—A liquid boiling at 347° F. (175° C.). It has a specific gravity at 0° C. of 0·9468.

(γ.) The third modification of this acid has not, as yet, been prepared. Its suggested formula is $CH(CH_3)(C_2H_5)CO.(OH)$ (methethacetic acid). Unlike the other acids, it rotates a ray of light to the right.

(δ.) *Tertiary valeric acid* (trimethacetic acid) $C(CH_3)_3CO(OH)$.

Preparation.—From tertiary butylic alcohol.

Properties.—A white crystalline body, melting at 95° F. (35° C.), and boiling at 321·8° F. (161° C.).

Valeric acid forms metallic and ethereal salts, called valerates, and also substitution compounds, such as chlorovaleric acid ($C_5H_7Cl_3O_2$).

Caproic Acid, $C_6H_{12}O_2=C_5H_{11}.CO(OH)$. *Molecular weight,* 116. *Sp. Gr. at* 32° F. (0° C.) 0·943. *Solidifies at* 15·8° F. (−9° C.) *Boils* at 388·4° F. (198° C.).

Synonym.—Hexylic acid.

Natural History.—It occurs as a glyceride in the butter of cow's milk, and also in cocoa-nut oil.

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Preparation.—(1.) By the action of alkalies on amyl cyanide ($C_5H_{11}.CN$).

(2.) By the oxidation of poppy oil, of casein, and of many fatty acids.

(3.) By the saponification of cocoa-nut oil, and distilling the soap formed with dilute sulphuric acid.

Properties.—A clear oil. It forms salts called *caproates.*

Leucine, or *Amido-caproic acid,* $C_6H_{13}NO_2$, or $C_6H_{11}(NH_2)O_2$, is formed by the decomposition of, or by the action of acids and alkalies on, various animal substances. It has not as yet been obtained from any caproic acid derivative. It consists of volatile crystalline scales, which melt at 212° F. (100° C.).

Œnanthylic Acid, $C_7H_{14}O_2$, or $C_6H_{13}CO(OH)$. *Molecular weight,* 130. *Sp. Gr. at* 32° F. (0° C.) 0·934. *Boils at* 413·6° F. (212° C.).

Synonym.—Heptylic acid.

Preparation.—By the oxidation either of castor oil or of œnanthylic aldehyde ($C_7H_{14}O$), a body obtained from castor oil by dry distillation.

Palmitic Acid, $C_{16}H_{32}O_2$, or $C_{15}H_{31}CO(OH)$. *Molecular weight,* 256.

Natural History.—It occurs in many, if not in most natural fats, as a glyceride, associated with stearin, as, *e.g.*, in palm oil, as glyceric palmitate; in spermaceti, as cetylic palmitate; in bees'-wax, as myricyl palmitate (melissin), etc.

Preparation.—(1.) By saponifying palm oil, and decomposing the soap formed with sulphuric acid.

(2.) By melting oleic acid with potassic hydrate.

Properties.—A colorless, odorless, tasteless body, insoluble in water. It forms normal, and in some cases (as with K and Na) acid metallic salts ($M'C_{16}H_{31}O_2$, or $M''(C_{16}H_{31}O_2)_2$.) It also forms ethereal salts, such as glyceryl palmitates or palmitins.

Margaric Acid, $C_{17}H_{34}O_2$, or $C_{16}H_{33}CO(OH)$. *Molecular weight,* 258.

History.—This was originally supposed to be a distinct acid, obtained by the saponification of natural fats. It is now proved, however, that what was originally called margaric acid, is simply a mixture of stearic with palmitic or other acids.

Preparation.—By the action of an alcoholic solution of potassic hydrate on cetyl cyanide, and decomposing the resulting potassium salt with dilute hydrochloric acid.

Stearic Acid, $C_{18}H_{36}O_2 = C_{17}H_{35}CO(OH)$. *Molecular weight,* 284.

Natural History.—A constituent of solid animal fats, such as suet. It always occurs in conjunction with palmitic acid. It is also found in certain vegetable fats, such as the fat of cacao beans, the berries of the cocculus Indicus, etc. It always occurs in nature as a glyceride.

Preparation.—The fat is first saponified with an alkali, and then

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decomposed by heating with dilute sulphuric acid. The free acid is then dissolved in alcohol and crystallized. It may be separated from palmitic acid as an insoluble magnesic stearate.

Properties.—A white crystalline body, melting at 156·5° F. (69·2° C.). It distils unchanged. It forms ethereal salts, and also metallic salts called stearates, most of which are insoluble.

See SUPPLEMENTARY CHAPTER FOR FATS, OILS, etc.

Lactic Series.

SERIES I. (*a.*)—*Formula* $C_nH_{2n}(OH)CO(OH)$.

The acids of this series are monobasic dihydric acids. They are derivatives of the acetic acid series, one of the hydrogens being substituted by one semi-molecule of hydroxyl. Thus—

$C_nH_{2n+1}CO(OH)$	—	$C_nH_{2n}(OH)CO(OH)$.
Acid of acetic series	—	Acid of lactic series.

Varieties.—(Each variety includes both normal and iso-acids.)

1. *Primary acids* $\begin{cases} C(C_nH_{2n+1})H.OH \\ CO.OH \end{cases}$
2. *Secondary acids* $\begin{cases} C(C_nH_{2n+1})_2.OH \\ CO.OH \end{cases}$
3. *Primary olefine acids* $C_nH_{2n} \begin{cases} CH_2\,OH \\ CO.OH \end{cases}$
4. *Secondary olefine acids* $C_nH_{2n} \begin{cases} C(C_nH_{2n+1})H.OH \\ CO.OH \end{cases}$
5. *Tertiary olefine acids* $C_nH_{2n} \begin{cases} C(C_nH_{2n+1})_2OH \\ CO.OH \end{cases}$

The following acids belong to the lactic series :—

NAME.	Formula.	Molecular Wt.
Carbonic acid	$CO(OH)_2 = CH_2O_3$	62
Glycollic acid	$CH_2(OH)CO(OH) = C_2H_4O_3$	76
Lactic acid	$C_2H_4(OH)CO(OH) = C_3H_6O_3$	90
Oxybutyric acid (Butylactic acid)	$C_3H_6(OH)CO(OH) = C_4H_8O_3$	114
Oxyvaleric acid (Valero-lactic acid)	$C_4H_8(OH)CO(OH) = C_5H_{10}O_3$	128
Leucic acid	$C_5H_{10}(OH)CO(OH) = C_6H_{12}O_3$	132
Amylhydro-oxalic acid	$C_6H_{12}(OH)CO(OH) = C_7H_{14}O_3$	146
Diamyloxalic acid	$C_{11}H_{22}(OH)CO(OH) = C_{12}H_{24}O_3$	216

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General Preparation of the Normal Acids of the Lactic Series.

(1.) *From the glycols* (*i.e.*, a dihydric alcohol, such as $C_2H_4(HO)_2$ (glycol)). By oxidation with nitric acid, platinum black, etc.

$$CH_2(OH).CH_2(OH) + O_2 = CH_2(OH)CO(OH) + H_2O.$$
Glycol + Oxygen = Glycollic acid + Water.

(2.) *From the monochlorinated or monobrominated acids of the acetic series.* By the action of argentic hydrate.

$$C_2H_4ClCO(OH) + AgHO = C_2H_4(OH)CO(OH) + AgCl$$
Chloropropionic acid + Argentic hydrate = Lactic acid + Argentic chloride.

(3.) *From the amidated derivatives of the acids of the acetic series.* By the action of nitrous acid.

$$CH_2(NH_2)CO(OH) + HNO_2 = CH_2(OH)CO(OH) + H_2O + N_2.$$
Amidoacetic acid + Nitrous acid = Glycollic acid + Water + Nitrogen.

(4.) *From the ketones and aldehydes of the acetic series.* By first digesting these bodies with hydrocyanic acid, and acting on the resulting cyanides with dilute hydrochloric acid.

The acids may be prepared as potassic salts,

(5.) By the action of a solution of potassic hydrate on the cyanides, or on the acid chlorides of the monochlorinated acids of the acetic series.

They may be prepared as ethylic salts of the secondary acids,

(6.) By the action of the zinc organo-metallic compounds on ethylic oxalate and the subsequent addition of water.

$$(\alpha.)\ \left\{\begin{matrix}CO.OC_2H_5\\CO.OC_2H_5\end{matrix}\right. + 2Zn(C_nH_{2n+1}) = \left\{\begin{matrix}C(C_nH_{2n+1})_2(OZnC_nH_{2n+1})\\CO.O\,C_2H_5\end{matrix}\right. + Zn\left\{\begin{matrix}C_nH_{2n+1}\\OC_nH_{2n+1}\end{matrix}\right.$$
Ethylic oxalate + Zinc compound.

$$(\beta.)\ \left\{\begin{matrix}C(C_nH_{2n+1})_2(OZnC_nH_{2n+1})\\CO.O\,C_2H_5\end{matrix}\right. + 2H_2O = \left\{\begin{matrix}C(C_nH_{2n+1})_2(OH)\\CO.OC_2H_5\end{matrix}\right. + Zn(OH)_2 + C_nH_{2n+2}$$
Secondary acid.

Properties (*General*).—All the acids of this series furnish *metallic salts* by their action on metallic carbonates; *ethereal salts*, by their action on alcohols; *acid chlorides*, by their action on phosphoric chloride; *acids of the acetic series*, by their action on hydriodic acid; and either *anhydrides* or *acids of the acrylic series*, by the action of heat.

Carbonic Acid; $CO(OH)_2 = H_2CO_3$. The constitution of this acid allies it to the lactic series, but unlike the other acids of the series it is *dibasic*.

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We need only note here that it forms:—

(α.) *Ethereal Salts*, such as, *e.g.*, ethylic carbonate $(C_2H_5)_2CO_3$. This is prepared by the action of argentic carbonate on ethylic iodide ($Ag_2CO_3+2C_2H_5I=2AgI + (C_2H_5)_2CO_3$). Ethylic carbonate is a colorless liquid, boiling at 257° F. (125° C.). Derivatives of this ether are known where the oxygen is wholly or partially replaced by sulphur, as, *e.g.*,

Ethylic monosulphocarbonic acid ... ... $(C_2H_5)H.CO_2S$.
Ethylic disulphocarbonic acid (*xanthic acid*) $(C_2H_5)HCOS_2$.
Ethylic trisulphocarbonic acid ... ... $(C_2H_5)HCS_3$,

(β.) *Amidogen Derivatives*, as, *e.g.*, *carbamic acid* $CO(NH_2)(OH)$, and *carbamide* (or *urea*) $CO(NH_2)_2$ from which latter body many compound ureas may be formed by the introduction of hydrocarbon groups in the place of hydrogen. When the oxygen, moreover, is replaced by sulphur, *sulpho-carbamide* or *sulpho-urea* ($CS(NH_2)_2$) is formed.

Glycollic Acid (*mono-oxy-acetic acid*) ($CH_2(OH)CO(OH) = C_2H_4O_3$). *Molecular weight*, 76. *Melts at* 176° F. (80° C.). *Boils at* 212° F. (100° C.).

Preparation.—(1.) By the general processes already described (page 606).

(2.) By the action of nascent hydrogen on oxalic acid.

$CO(OH)CO(OH)$	+	$2H_2$	=	$CH_2(OH)CO(OH)$	+	H_2O.
Oxalic acid	+	Hydrogen	=	Glycollic acid	+	Water.

Properties.—These vary somewhat according to its preparation. It is a white crystalline solid, soluble in water, in alcohol, and in ether. It is decomposed by a heat of 302° F. (150° C.). It yields oxalic acid by oxidation, and paramalic acid by dehydration.

Lactic Acid; $C_2H_4(OH)CO(OH) = C_3H_6O_3$. There are at least two, and possibly more modifications of this acid.

(α.) *Ordinary lactic acid* ($CH_3.CH(OH)CO(OH)$). This acid is produced (1) by the lactic acid fermentation; (2) by the oxidation of propene glycol; (3) by the action of argentic hydrate on chloropropionic acid; (4) by the action of nascent hydrogen on pyruvic acid; and (5) by the action of hydrocyanic acid on acetic aldehyde, and the subsequent digestion of the cyanide formed with hydrochloric acid.

(β.) *Paralactic* or *ethylene lactic acid* ($CH_2(OH)CH_2.CO(OH)$). This is prepared by decomposing paralactyl chloride (formed by combining ethene with carbonyl chloride) with an alkali. It may also be obtained from the gastric juice, from the saliva of diabetic patients, from various secretions, and also from muscle, by the action of cold water or of dilute alcohol.

Properties.—Lactic acid has never been obtained in the solid state, but its solution may be concentrated until it becomes a thick, colorless, syrupy liquid, having a specific gravity of 1·215. It is very

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acid and very soluble in water, alcohol, and ether. By the action of a continuous heat upon it, *lactide*, or *lactic anhydride* ($C_3H_4O_2$) is formed. This body is a white crystalline substance, melting at 256·1° F. (124·5° C.), combining with water to form *lactic acid*, and with ammonia to form *lactamide* ($C_2H_4(OH)CO(NH_2)$).

Heated with *dilute sulphuric acid*, lactic acid forms aldehyde and formic acid; heated with *hydriodic acid*, it is reduced to propionic acid ($C_3H_6O_3 + 2HI = C_3H_6O_2 + H_2O + I_2$): by *oxidation*, it yields acetic acid, formic acid, and carbonic anhydride; by the action of *phosphoric chloride*, it forms chloro-propionic chloride ($C_2H_4ClCOCl$). All the lactates are soluble.

Lactic acid may be known from glycollic acid by its yielding no precipitate with plumbic acetate.

Paralactic acid by oxidation yields malonic acid. Varieties of this acid are said to have different actions on a polarized beam of light.

Pyruvic Series.

SERIES I. (β.)—*Formula* $C_nH_{2n-1}O.CO(OH)$.

The acids of this series are monobasic and dihydric. They may be regarded as derivatives of the lactic acid series by the abstraction of H_2. Thus—

$C_nH_{2n}(OH)CO(OH)$;	$C_nH_{2n-1}O.CO(OH)$.
Acid of lactic series;	Acid of pyruvic series.

It includes—

NAME.	Formula.	Molecular Wt.	Remarks.
Glyoxalic acid	$C_2H_2O_3$	74	
Pyruvic acid (Pyroracemic acid)	$C_3H_4O_3$	88	A liquid prepared by the dry distillation of tartaric, glyceric or racemic acids. Boils at 329° F. (165° C.). With sodium amalgam or with HI (*i. e.* by nascent hydrogen) it forms lactic acid.
Epihydric acid	$C_4H_6O_3$	102	
Acetopropionic acid	$C_5H_8O_3$	116	
Convolvulinoleic acid	$C_{13}H_{24}O_3$	228	By the action of acids or alkalies on certain glycerides contained in the tubers of the jalap and the convolvulus orizabensis.
Jalapinoleic acid	$C_{16}H_{30}O_3$	270	
Ricinoleic acid	$C_{18}H_{34}O_3$	298	The glyceride of this acid is the chief constituent of castor oil. It is a yellow inodorous oil, becoming solid at 32° F. (0° C.).

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Glyoxylic Series.

SERIES I. (γ.)—*Formula* $C_nH_{2n-1}(OH)_2CO.OH$.

The acids of this series are monobasic and trihydric. They are derivatives of triatomic alcohols. Thus—

$C_3H_8O_3$	—	$C_3H_6O_4$.
Glycerin	—	Glyceric acid.

It includes—

Name.	Formula.	Molecular Wt.	Remarks.
Glyoxylic acid .. (Dioxyacetic acid)	$CH(OH)_2CO(OH)=C_2H_4O_4$	92	Prepared by the oxidation of glycol and of alcohol, and by the action of nascent hydrogen on oxalic acid. A colorless syrup; distils at 212° F. (100° C.) without change. Dissolves zinc without the evolution of hydrogen.
Glyceric acid .. (Dioxypropionic acid)	$CH_2(OH).CH(OH).CO(OH)$ $=C_3H_6O_4$	106	Prepared by the action of nitric acid on glycerine, and by the spontaneous decomposition of nitro-glycerin. A thick syrup, forming iodopropionic acid ($C_3H_5IO_2$), when the product formed with phosphorus iodide is treated with water.

Acrylic Series.

SERIES II.—*Formula* $C_nH_{2n-1}CO(OH)$.

The acrylic series of acids are mostly oily liquids, the primary acids existing as glycerides in natural fats and oils. They are monobasic, that is their salts are formed by the substitution of one equivalent of a metal for one of hydrogen. Fused with potassic hydrate, they eliminate hydrogen and form potassic acetate and a potassic salt of another acid—

$C_{18}H_{34}O_2$	+	$2KHO$	=	$C_2H_3KO_2$	+	$C_{16}H_{31}KO_2$	+	H_2.
Oleic acid	+	Potassic hydrate	=	Potassic acetate	+	Potassic palmitate	+	Hydrogen.

Nascent hydrogen converts them into the acids of the acetic series.

This series includes :—

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Name.	Formula.	Remarks.
Acrylic acid	$C_2H_3CO(OH)$	*Preparation.*—By the oxidation of acrolein C_3H_4O. A colorless liquid freezing at 44·6° F. (7° C.), and boiling at 284° F. (140° C.). By the action of nascent hydrogen, it is converted into propionic acid ($C_3H_6O_2$), and by the action of bromine into dibromopropionic acid.
Crotonic acid.. ..	$C_3H_5CO(OH)$	It was supposed to be the acid obtained by the saponification of croton oil, but this is doubtful. It is prepared by the oxidation of crotonic aldehyde. It is a white crystalline body melting at 161·6° F. (72° C.), and boiling at 357·8° F. (181° C.), evolving hydrogen when heated with potassic hydrate.
Angelic acid	$C_4H_7CO(OH)$	Found in angelica or sumbul root, and also prepared by heating oil of camomile (angelic aldehyde) with potassic hydrate. A crystalline solid, melting at 113° F. (45° C.), and boiling at 374° F. (190° C.).
Pyroterebic acid ..	$C_5H_9CO(OH)$	A liquid boiling at 410° F. (210° C.) prepared by the distillation of terebic acid.
Damaluric acid ..	$C_7H_{12}O_2$	Acids existing in the urine of cows and horses.
Damolic acid.. ..	$C_{12}H_{24}O_2$	
Moringic acid	$C_{15}H_{28}O_2$	Present in the oil of ben, together with stearic acid, etc.
Cimicic acid ..		A yellow crystalline acid extracted from a kind of bug.
Physetoleic acid ..	$C_{16}H_{30}O_2$	A crystalline acid obtained from sperm oil. It melts at 86° F. (30° C.).
Hypogæic acid ..	$C_{16}H_{30}O_2$	Exists as a glyceride in earth-nuts with palmitic acid, etc. It melts at 93·2° F. (34° C.)
Gaïdic acid	$C_{16}H_{30}O_2$	Colorless crystals, melting at 100·4° F. (38° C.), prepared by the action of nitrous acid on hypogæic acid.
Oleic acid	$C_{18}H_{34}O_2$	An acid present as a glyceride (olein) in most natural fats and non-drying oils (*see* Candles). Crystallizes in white needles, which melt at 57·2° F. (14° C.). Specific gravity at 66·2° F. (19° C.) 0·898. Insoluble in water; soluble in alcohol, ether, and in sulphuric acid. Nitric acid converts it into acids of the acetic series, and nitrous acid converts it into elaidic acid. The solid acid is oxidized slowly, and the liquid acid rapidly, by exposure to air. Fused with potassic hydrate it yields acetate and palmitate of potassium.
Elaidic acid	$C_{18}H_{34}O_2$	By the action of nitrous acid on oleic acid. A crystalline body melting at 111·2° F. (44° C.).
Doeglic acid	$C_{19}H_{36}O_2$	An acid prepared from the oil obtained from the doegling or bottle-nose whale.
Brassic acid	$C_{22}H_{42}O_2$	An acid obtained from the oil of a species of brassica (colza).
Erucic acid	$C_{22}H_{42}O_2$	An acid from the oil of the black mustard.
Secondary Acids.		
Methacrylic acid ..	$C_3H_5CO(OH)$	An acid isomeric with crotonic acid. A colorless oily liquid, prepared by the action of phosphorous chloride on ethylic dimethoxylate. Fused with potash, it yields hydrogen and potassic propionate and formate.
Methylcrotonic acid	$C_4H_7CO(OH)$	
Ethylcrotonic acid	$C_5H_9CO(OH)$	

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Sorbic Series.

SERIES III.—*Formula* $C_nH_{2n-3}CO(OH)$.

This includes:—

Name.	Formula.	Molecular Weight.	Fusing Point.		Occurrence and Preparation.
			° F.	° C.	
Tetroleic acid	$C_3H_3CO(OH)=C_4H_4O_2$	84	168·8	76·0	Prepared by the action of potassic hydrate on chloro-crotcnic acid.
Sorbic acid	$C_5H_7CO(OH)=C_6H_8O_2$	112	273·2	134·0	Found in mountain ash berries.
Stearolic acid	$C_{17}H_{31}CO(OH)=C_{18}H_{32}O_2$	280	118·4	48·0	Prepared by the action of potassic hydrate on bromoleic acid.

Benzoic Series.

SERIES IV.—*Formula* $C_nH_{2n-7}CO(OH)$.

Preparation.—(1.) By the oxidation of the corresponding aldehydes and alcohols. Thus benzoic acid may be obtained either from benzoic aldehyde (C_6H_5CHO), or from benzylic alcohol ($C_6H_5CH_2OH$).

(2.) By the action of alkalies on the nitriles (abnormal cyanides).

$$C_6H_5CN + KHO + H_2O = C_6H_5CO(OK) + NH_3.$$

Benzonitrile + Potassic hydrate + Water = Potassic benzoate + Ammonia.

(3.) By the action of water on the corresponding acid chlorides.

(4.) By the action of sodium and carbonic anhydride on the monobrominated derivatives of the C_nH_{2n-6} series of hydrocarbons—

$$C_6H_5Br + Na_2 + CO_2 = C_6H_5CO(ONa) + NaBr.$$

Bromobenzene + Sodium + Carbonic anhydride = Sodic benzoate + Sodic bromide.

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This series includes :—

Name.	Formula.	Mol. Wt.	Melting Pt.		Boiling Pt.		
			° F.	° C.	° F.	° C.	
Phenoic acid ..			140·0	60·0			
Collinic acid ..	$C_5H_3CO(HO)$ $=C_6H_4O_2$	108	206·6	97·0			
Benzenic acid..			230·0	110·0	455·0	235·0	
Benzoic acid ..	$C_6H_5CO(OH)$ $=C_7H_6O_2$	122	250·5	121·4	462·2	239·0	Present in gum benzoin and in other gums. *Preparation. See* General methods. Also (1) by the oxidation of a mixture of benzene and formic acid; (2) by boiling hippuric acid with hydrochloric acid; (3) By the oxidation of certain organic bodies, as casein, gelatin, etc. *Properties.* Feathery crystals, soluble in alcohol and boiling water. *Nitric acid* has no action upon it. With *fuming nitric acid* it forms a substitution product. With the *haloids* it also forms substitution products. With PCl_5 it forms benzoic chloride. With *nascent hydrogen* it forms hydrobenzoic acid $C_6H_9CO(OH)$.
Toluic acid ..	$C_6H_4(CH_3)CO(OH)$ $=C_8H_8O_2$	136	347·0	175·0			Exists in three modifications: (1.) *Paratoluic.* (2.) *Metatoluic.* (3.) *Orthotoluic.* A crystalline body with similar reactions to benzoic acid.
Alphatoluic acid	$C_6H_5CH_2CO(OH)$ $=C_8H_8O_2$	136	169·7	76·5	509·0	265·0	Prepared by General Process 2. A crystalline body.
Xylic acid .. (Xylilic acid)	$C_6H_3(CH_3)_2CO(OH)$ $=C_9H_{10}O_2$	150	248·0	120·0	523·4	273·0	Exists in two forms, as xylic and paraxylic acids.
Alphaxylic acid	$C_6H_4\{^{CH_3}_{CH_2CO(OH)}$ $=C_9H_{10}O_2$	150	107·6	42·0			
Cumylic acid ..	$C_6H_2(CH_3)_3CO(OH)$ $=C_{10}H_{12}O_2$	164	302·0	150·0			
Cumic acid ..	$C_6H_4(C_3H_7)CO(OH)$ $=C_{10}H_{12}O_2$	164	197·6	92·0			
Homocumic acid	$C_6H_4\{^{C_3H_7}_{CH_2CO(OH)}$ $=C_{11}H_{14}O_2$	178	125·6	52·0			

Some of the derivatives of benzoic acid need further notice.

Benzoic Chloride; *Benzoyl chloride* (C_7H_5OCl).

Preparation.—By the action of phosphorus pentachloride on benzoic acid.

Properties.—A colorless, pungent liquid. Specific gravity 1·106. Its vapor is heavy, and burns with a greenish flame.

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Benzoic Anhydride or **Oxide** ($C_{14}H_{10}O_3$).

Preparation.—By the action of benzoyl chloride on potassic benzoate ($C_7H_5O(ONa) + C_7H_5OCl = (C_7H_5O)_2O + NaCl$).

Properties.—It forms oblique rhombic prisms, melting at 42° C.

Benzoic peroxide ($C_{14}H_{10}O_4$).

Chlorobenzoic Acid, $C_6H_4Cl.CO(OH)$.

Preparation.—By the action of potassic chlorate and hydrochloric acid on benzoic acid.

Bromobenzoic Acid, $C_6H_4BrCO(OH)$.

Preparation.—By the action of bromine on argentic benzoate.

Nitrobenzoic Acid, $C_6H_4(NO_2)CO(OH)$.

Preparation.—By boiling benzoic acid in fuming nitric acid.

Properties.—A crystalline substance.

Hippuric or **Benzamidacetic Acid** ($C_9H_9NO_3$).

Natural History.—Hippuric acid occurs as a potassium and sodium salt in the urine of horses, cows, etc., and also in human urine, more especially after the administration of benzoic acid.

In preparing the acid from urine it is necessary that it should be fresh, otherwise it evolves ammonia, benzoic acid being formed by the action of heat on the hippuric acid.

Preparation.—By the action of the zinc salt of amidacetic acid on benzoic chloride.

Properties.—The acid crystallizes in slender prisms. It melts when heated, and at a high temperature is decomposed, forming benzoic acid, benzonitrile, etc. It is slightly soluble in water (1 in 400 at 60° F.), and in hot alcohol.

Its reaction is acid. With hot sulphuric acid, it yields benzoic acid; with hot hydrochloric acid, amidacetic acid and benzoic acid; with nitric acid, benzoglycollic acid with the evolution of nitrogen.

It is monobasic, and forms salts called hippurates.

Oxybenzoic or Salicylic Series.

SERIES IV. (a.)—*Formula* $C_nH_{2n-8}(OH)CO(OH)$.

The acids of this series are monobasic and dihydric. They are related to benzoic acid in the same manner as the lactic series is related to the acetic series.

It includes—

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Name.	Formula.	Preparation and Properties.
Salicylic acid (orthoxybenzoic acid)	$C_6H_4(OH)CO(OH)$ $=C_7H_6O_3$	*Preparation.*—(1.) By passing CO_2 into phenol containing small pieces of sodium. (2.) By melting salicin or coumaric acid with potassic hydrate ($C_7H_8O_2+KHO$ $=C_7H_5KO_3+H_2$). (3.) By distilling oil of wintergreen with potash. *Properties.*—A crystalline body, melting at 368·6° F. (187° C.), decomposed at 428° F. (220° C.), evolving phenol. Dissolves in cold water (1 in 1,000). With PCl_5 it forms chlorobenzoic chloride. Its solution gives a violet color to ferric salts.
Oxybenzoic acid (metoxybenzoic acid)	do.	*Preparation.*—By the action of nitrous acid on amido benzoic acid. *Properties.*—A crystalline body, melting at 390·2° F. (199° C.). Requires a high temperature to decompose it. It gives no violet color with ferric salts.
Paraoxybenzoic acid ..	do.	Prepared by heating anisic acid with HI. Soluble in water (1 in 126 at 60° F.) Melts at 410° F. (210° C.) With ferric salts gives a yellow precipitate.
Anisic acid	$C_8H_8O_3$	Prepared by oxidizing anisic aldehyde ($C_8H_8O_2$) or crude oil of aniseed. Colorless crystals, melting at 347° F. (175° C.). Soluble in alcohol, ether, and hot water.
Cresotic acid (carbocresylic acid)	$C_6H_3(OH)\begin{cases}CH_3\\CO(OH)\end{cases}$	Prepared by the action of CO_2 and Na on cresol (C_7H_8O). *Orthocresotic acid* melts at 237·2° F. (114° C.); *paracresotic acid* at 298·4° F. (148° C.), and *metacresotic acid* at 338° F. (170° C.). They all produce a deep violet color with ferric chloride.
Oxymethylbenzoic acid	$C_6H_4\begin{cases}CH_2(OH)\\CO(OH)\end{cases}$	
Mandelic acid (formobenzoic)	$CH(OH)\begin{cases}C_6H_5\\CO(OH)\end{cases}$	Prepared by the action of HCl on bitter almond oil.
Phloretic acid	$C_2H_4\begin{cases}C_6H_4(OH)\\CO(OH)\end{cases}$	Melts at 264·2° F. (129° C.). Prepared by the action of potash on phloretin. *Phloretic acid* gives a *green* color with ferric chloride, whilst *isophloretic acid* has no action.
Hydrocoumaric acid ..		
Hydroparacoumaric acid		
Phenyllactic acid	$C_2H_3(OH)\begin{cases}C_6H_5\\CO(OH)\end{cases}$	
Thymylcarbonic acid or thymotic acid	$C_6H_2(OH)\begin{cases}C_3H_7\\CH_3\\CO(OH)\end{cases}$	*Preparation.*—By the action of CO_2 and Na on thymol. It melts at 248° F. (120° C.), and gives a blue color with ferric chloride.

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Dioxybenzoic Series.

SERIES IV. (β.)—*Formula* $C_nH_{2n-9}(OH)_2CO(OH)$.

These are monobasic acids, and include—

Names.	Formula.	Preparation and Properties.
Pyrocatechuic acid .. Carbo-hydroquinonic acid.		Prepared by melting potash either with piperic or quinic acid, or with kino, catechu, etc. When the acid is heated, it yields CO_2 and pyrocatechin.
Oxy-salicylic acid ..	$C_6H_3(OH)_2CO(OH)$	By the action of potash on iodo-salicylic acid. It melts at 379·4° F. (193° C.), and is decomposed at 418·6° F. (212° C.), yielding anthrachrysone. It is soluble in water, alcohol, and ether. It strikes a deep blue with ferric chloride.
Dioxybenzoic acid ..	$C_6H_3(SO_3H)_2CO(OH)$	

Gallic Series.

SERIES IV. (γ.)—*Formula* $C_nH_{2n-10}(OH)_3CO(OH)$.

Gallic Acid (*Trioxybenzoic acid*) $C_6H_2(OH)_3CO(OH) = C_7H_6O_5$. *Molecular weight*, 170.

Natural History.—It is found in gall nuts, acorns, hellebore root, black and green tea, etc.

Preparation.—By the action of argentic hydrate on di-iodo-salicylic acid.

Properties.—(α.) *Physical.* A white crystalline body ($C_7H_6O_5.OH_2$) having a powerful astringent taste. At 419° F. (215° C.) it is decomposed into CO_2 and pyrogallic acid ($C_6H_6O_3$), whilst by a heat of 480·2° F. (249° C.) it is resolved into carbonic anhydride, water and metagallic acid ($C_6H_2O_2$). It is soluble in water (1 in 100 at 60° F., and 1 in 3 at 212° F.).

(β.) *Chemical.*—The solution has an acid reaction and rapidly decomposes. It does not precipitate gelatine. It forms a black precipitate with iron salts, the color disappearing by heat in the case of ferric salts, but not in the case of ferrous salts. It is readily oxidized, and hence rapidly reduces gold and silver salts. When boiled with a solution of arsenic acid, tannic acid is formed.

(For the TANNINS *see* SUPPLEMENTARY CHAPTER.)

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Cinnamic Series.

SERIES V.—*Formula* $C_nH_{2n-9}CO(OH)$.

This series is monobasic. The cinnamic series is related to the benzoic series in a similar manner as the acrylic is related to the acetic series of acids. Thus :—

$C_nH_{2n+1}CO(OH)$ — $C_nH_{2n-1}CO(OH)$;
Acetic — Acrylic.

$C_nH_{2n-7}CO(OH)$ — $C_nH_{2n-9}CO(OH)$
Benzoic — Cinnamic.

It includes—

Acids.	Formula.	Molecular Weight.	Melting Point. ° F.	Melting Point. ° C.	
Cinnamic	$C_8H_7CO(OH)$	148	248·0	120·0	*Preparation.*—(1.) By heating benzoic aldehyde with acetic chloride ($C_7H_6O + C_2H_3OCl = HCl + C_9H_8O_2$). (2.) By the oxidation of cinnamon oil. It is present ready formed in the balsams of Peru and Tolu. *Properties.*—A crystalline body, boiling at 559·4° F. (293° C.). Soluble in alcohol, not very soluble in water. With *nitric* or with *chromic acid* it forms benzoic acid and benzoic aldehyde. With *nascent hydrogen* (water and sodium amalgam), or heated with *hydriodic acid*, it forms hydrocinnamic acid ($C_9H_{10}O_2$). Fused with *potassic hydrate* it forms potassic benzoate and acetate. By *heat* it forms CO_2 and cinnamene (C_8H_8).
Atropic	ditto	148	222·8	106·0	Formed together with tropine ($C_8H_{15}(NO)$) from atropine, by the action of alkalies.
Isatropic	ditto	148	392·0	200·0	

SERIES V. (α.)—*Formula* $C_nH_{2n-11}CO(OH)$.

This includes phenyl-propiolic acid, $C_6H_5C_2CO(OH)$, a crystalline acid melting at 276·8° F. (136° C.). It is prepared by the action of potassic hydrate on bromocinnamic acid, and is converted by nascent hydrogen into hydrocinnamic acid.

Naphtoic Series.

SERIES VI.—*Formula* $C_nH_{2n-13}CO(OH)$.

This series includes two isomeric acids, *viz.*, α-naphtoic acid, and β-naphtoic acid. The former melts at 320° F. (160° C.), and the

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latter at 359·6° F. (182° C.). By the action of sodium and carbonic anhydride on α- and β-naphtol, the two isomeric acids α- and β-oxy-naphtoic acids are formed.

SERIES VI. (α.)—*Formula* $C_nH_{2n-19}CO(OH)$.

This includes *anthracene carboxylic acid*, $C_{14}H_9CO(OH)$, a solid body, melting at 402·8° F. (206° C.). It is prepared by heating anthracene with carbonic oxychloride. When heated it yields anthracene and carbonic anhydride.

B.—DIBASIC ACIDS.

That is acids containing two semi-molecules of carboxyl (COOH).

Succinic Series.

SERIES I.—*Formula* $C_nH_{2n}(COOH)_2$.

Preparation (general).—(1.) By the oxidation of many fatty organic bodies, such as suet, etc., with nitric acid.

$C_4H_8O_2$	+	O_3	=	H_2O	+	$C_4H_6O_4$.
Butyric acid	+	Oxygen	=	Water	+	Succinic acid.

(2.) By the oxidation of the primary glycols.

$C_2H_4(OH)_2$	+	$2O_2$	=	$2H_2O$	+	$C_2O_2(OH)_2$.
Glycol	+	Oxygen	=	Water	+	Oxalic acid.

(3.) By the action of potassic hydrate or hydrochloric acid on the the nitriles (cyanides) of the dyad radicals.

$$\left\{\begin{matrix} C_nH_{2n}(CN) \\ C_nH_{2n}(CN) \end{matrix}\right. + 2KHO + 2H_2O = \left\{\begin{matrix} C_nH_{2n}(COKO) \\ C_nH_{2n}(COKO) \end{matrix}\right. + 2NH_3$$

(4.) By the action of sodium or silver on the iodo-derivatives of the acetic acid series. Thus :—

$$2C_nH_{2n}ICO(OH) + Ag_2 = C_{2n}H_{4n}(COOH)_2 + 2AgI.$$

Properties (general).—These dibasic acids are all crystalline solids, yielding by heat either the anhydride and water, or carbonic anhydride and an acid of the acetic series.

Thus it will be noted that the acids of the succinic series are related to the *glycols*, as seen by the second method of preparation described above; to the *dyad radicals*, as seen by the third method, and by the further fact that in some cases they yield the hydride of the radical, when heated with an excess of caustic baryta; and also to the *acids of the acetic series*, as seen by the fourth method of preparation, whilst conversely, in some cases, the succinic series may be converted into the acetic, by the abstraction of carbonic anhydride.

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This series includes—

Names.	Formula.	Molecular Weight.	Melting Pt.		Boiling Pt.		Remarks.
			° F.	° C.	° F.	° C.	
Oxalic	$(COOH)_2$	90					See below.
Malonic.. ..	$CH_2(COOH)_2$	104	284·0	140			Prepared by the oxidation of malic acid and of propene glycol. Decomposed at 302° F. (150° C.).
Succinic ..	$C_2H_4(COOH)_2$	128	356·0	180	455	235	See page 620.
Pyrotartaric	$C_3H_6(COOH)_2$	132	233·6	112			Prepared by heating tartaric acid. It volatilizes at 392° F. (200° C.)
Adipic	$C_4H_8(COOH)_2$	146	284·0	140	)		By the oxidation of fats with nitric
Pimelic ..	$C_5H_{10}(COOH)_2$	160	273·2	134	)		acid.
Suberic ..	$C_6H_{12}(COOH)_2$	174	257·0	125			Prepared by the oxidation of cork with nitric acid, and by the action of nitric acid on certain fats. Fusible and volatile.
Anchoic .. (Separgylic)	$C_7H_{14}(COOH)_2$	188	240·8	116			By the action of nitric acid on Chinese wax, and on the fatty acids of cocoa nut oil.
Sebacic.. ..	$C_8H_{16}(COOH)_2$	202	260·6	127			Prepared by the destructive distillation of oleic acid.
Rocellic ..	$C_{15}H_{30}(COOH)_2$	300	269·6	132			Present in certain lichens. Volatile at 392° F. (200° C.).

Oxalic Acid.—$(COOH)_2=C_2H_2O_4$; (crystals$=C_2H_2O_4,2H_2O$).

Natural History.—Oxalic acid is present in most plants, either in a free state, or as a lime or alkaline oxalate. It occurs very frequently as a lime-salt in the urine (mulberry calculus). Its formation in this latter case is no doubt due to some imperfection in the normal oxidising process going on in the body, the carbon and hydrogen not being converted, as usual, into water and carbonic anhydride.

Preparation.—(1.) By the oxidation of organic compounds, such as sawdust, sugar, etc., either by the action of nitric acid, or by their fusion with potassic hydrate, whereby a potassic oxalate is formed.

$C_{12}H_{22}O_{11}$	+	O_{18}	=	$6C_2H_2O_4$	+	$5H_2O$
Sugar	+	Oxygen	=	Oxalic acid	+	Water.

(2.) By the direct combination of an alkaline metal with carbonic anhydride.

$2CO_2$	+	Na_2	=	$Na_2C_2O_4$.
Carbonic anhydride	+	Sodium	=	Sodic oxalate.

(3.) By the decomposition of cyanogen with water.

C_2N_2	+	$4H_2O$	=	$C_2H_2O_4$	+	$2NH_3$.
Cyanogen	+	Water	=	Oxalic acid	+	Ammonia.

(4.) By the action of heat on potassic formate ($2HCO(OK)=H_2+K_2C_2O_4$).

(5.) By the oxidation of ethylene glycol (*see* page 617).

Commercial preparation of oxalic acid.—A thick paste is first prepared by mixing sawdust with a solution containing potassic hydrate (1 equiv.) and sodic hydrate (2 equiv.), the alkaline solution having a specific gravity of 1·35. This paste is then heated on iron plates at 400° F. (204° C.) for some hours, whereby hydrogen is evolved from the decomposition

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of the water of the alkaline hydrates, whilst the oxygen liberated oxidises the sawdust. The grey mass formed contains about one-fourth its weight of oxalic acid. This is then treated with water, which leaves the oxalate of soda undissolved, owing to its insolubility in water. The insoluble residue, after the action of the water, is then boiled with lime, and the resulting calcic oxalate decomposed with sulphuric acid. The clear liquor containing the oxalic acid is then evaporated down and crystallised.

The sawdust yields on an average about half its weight of crystallised oxalic acid.

The alkalies are recovered from the liquid with which the mass is first treated by evaporating the solution to dryness, calcining the residue, in order to destroy any organic matter present, and afterwards decomposing the carbonates with calcic hydrate. The recovered alkalies may then be used for a new operation.

Properties.—(a.) *Physical.* Oxalic acid consists of colorless crystals (oblique rhombs). At a heat of 212° F. (100° C.) the water of crystallisation is driven off; at 320° F. (160° C.) the acid sublimes, but at a temperature above this it is decomposed into formic acid and carbonic anhydride ($C_2H_2O_4 = CH_2O_2 + CO_2$), the formic acid being afterwards further decomposed by heat into water and carbonic oxide ($CH_2O_2 = CO + H_2O$). It is soluble in water (1 in 8 at 60° F., and 1 in 1 at 212° F.), and also in alcohol. The acid is poisonous. Chalk and magnesia constitute the proper antidotes.

(a.) *Chemical.* The solution of oxalic acid is very acid to litmus. *Sulphuric acid* converts it into H_2O, CO_2 and CO. *Nitric acid* acts slowly upon it, converting it into CO_2. Heated with *alkalies*, it yields hydrogen and an alkaline carbonate.

Uses.—In calico-printing; in cleansing brass and leather; also as a solvent for Prussian blue in the manufacture of blue ink.

It forms salts called oxalates, a few of which we note as follows:—

	Names.	Formula.	Solubility in water.		Remarks.
			° F.	212° F.	
Potassium oxalates.	Neutral	$C_2K_2O_4 2aq$	1 in 3		
	Acid (binoxalate or salt of sorrel)	$C_2HKO_4 2aq$	1 in 40	1 in 6	
	Hyperacid or quadroxalate	$C_2HKO_4, C_2H_2O_4, 2aq$			
	Sodic oxalate		almost not very	insoluble very	
Ammonium oxalates.	Neutral	$C_2(NH_4)_2O_4 2aq$			Yields by heat oxamide; heated with phosphoric anhydride it forms cyanogen.
	Acid(binoxalate)	$C_2H(NH_4)O_4 aq$			Yields oxamic acid by heat.
	Calcic oxalate	$C_2Ca''O_4 4aq$	insoluble		
	Ferrous oxalate	$C_2Fe''O_4$	insoluble		
	Ferric oxalate	$Fe_2(C_2O_4)_3 3aq$	very soluble		
	Ethyl (oxalic ether)	$(C_2H_5)_2C_2O_4$			Sp. Gr. 1·09. Boils at 183·8° F. (84·3° C.).
	Acid ethyl oxalate or ethyl-oxalic acid	$(C_2H_5)C_2HO_4$			

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All the oxalates are decomposed by heat. The alkaline and the earthy oxalates, if not too strongly heated, evolve CO, and leave carbonates of the metals, whilst the oxalates of other metals leave metallic oxides. With sulphuric acid the oxalates break up into CO and CO_2, leaving a residue of sulphate, which residue, however, does not blacken by the action of the acid, inasmuch as no separation of carbon takes place.

Succinic Acid.—$C_2H_4(COOH)_2=C_4H_6O_4$. [*Molecular weight*, 128. *Fuses at* 356° F. (180° C.). *Boils at* 455° F. (235 °C.).]

Natural History.—It is found in amber, in some lignites, and occasionally in animal and vegetable substances.

Preparation.—(1.) By the action of potassic hydrate on ethylene cyanide—

$$\underset{\text{Ethylene cyanide}}{C_2H_4(CN)_2} + \underset{\text{Water}}{4H_2O} = \underset{\text{Ammonia}}{2NH_3} + \underset{\text{Succinic acid.}}{C_4H_6O_4}.$$

(2.) By the oxidation of butyric acid—

$$\underset{\text{Butyric acid}}{C_4H_8O_2} + \underset{\text{Oxygen}}{O_3} = \underset{\text{Water}}{H_2O} + \underset{\text{Succinic acid.}}{C_4H_6O_4}.$$

(3.) By the action on malic acid, either of (α) nascent hydrogen, or (β) fermentation (*see* p. 489), or (γ) hydriodic acid.

(α.) $C_4H_6O_5 + H_2 = H_2O + C_4H_6O_4$.

(γ.) $C_4H_6O_5 + 2HI = H_2O + I_2 + C_4H_6O_4$.

Properties.—Colorless crystals (oblique rhombs). It melts at 356° F. (180° C.), and boils at 455° F. (235° C.), water and succinic anhydride ($C_4H_4O_3$) being formed. [*Iso-succinic acid* melts at 266° F. (130° C.), and boils at 302° F. (150° C.), forming CO_2 and propionic acid ($C_3H_6O_2$).]

It is soluble in water (1 in 5 at 60° F., 1 in 3 at 212° F.). With nascent oxygen it yields ethylene, CO_2, and H_2O; ($C_4H_6O_4+O=C_2H_4+2CO_2+H_2O$). Nitric and hydrochloric acids have no action upon it. Distilled with H_2SO_4 and MnO_2, it yields acetic acid.

Distinctive Reactions of Succinic Acid.—*Succinic acid* (as a sodic salt) gives a red-brown precipitate with ferric chloride. *Isosuccinic acid* gives none.

Succinic acid is not precipitated from its salts by the mineral acids. It gives a white precipitate with $BaCl_2$, on the addition of an alcoholic solution of ammonia. *Benzoic acid* is precipitated from its salts by the mineral acids. It gives no precipitate with $BaCl_2$.

Malic Series.

SERIES I. (α.)—*Formula* $C_nH_{2n-1}(OH)(CO.OH)_2$.

These acids are trihydric and dibasic:—

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Names.	Formula.	Remarks.
Tartronic .. .. (oxymalonic).	$CH(OH)(COOH)_2 = C_3H_4O_5$	*Preparation.*—By the spontaneous decomposition of nitro tartaric acid.
Malic.. .. .. .. (Oxysuccinic).	$C_2H_3(OH)(COOH)_2 = C_4H_6O_5$	Malic acid is widely distributed in plants as in the juices of apples, pears, etc. (with citric acid), or of rhubarb (with acid potassic oxalate), or in the berries of the mountain ash, or in tobacco leaves (as bimalate of lime). *Preparation.*—(1.) From the above juices. (2.) By the action of nitrous acid on asparagine ($C_4H_8N_2O_3$) and on aspartic acid ($C_4H_7NO_4$), bodies found in the asparagus, the marsh mallow, etc. ($C_4H_8N_2O_3$ asparagine + $2HNO_2 = C_4H_6O_5 + 2H_2O + 2N_2$). (3.) By the action of argentic hydrate on monobromo-succinic acid. *Properties.*—Crystalline, soluble in water and in alcohol. With *ferments*, such as putrifying cheese, it yields CO_2, succinic and acetic acids; digested with *hydriodic acid* in sealed tubes, it yields succinic acid; fused with *potassic hydrate*, or boiled with a *strong mineral acid*, it yields sorbic acid.
Citramalic.. ..	$C_3H_5(OH)(COOH)_2$	
Glutanic	$C_3H_5(OH)(COOH)_2$	*Preparation.*—By the action of nitrous acid on glutamic acid, obtained by heating casein, etc., with hydrochloric acid.
Oxyadipic	$C_4H_7(OH)(COOH)_2$	
Oxysuberic ..	$C_6H_{11}(OH)(COOH)_2$	

Tartaric Series.

Series I. (β.)—*Formula* $C_nH_{2n-2}(OH)_2(COOH)_2$.

These acids are tetrahydric and dibasic:—

Names.	Formula.	Remarks.
Mesoxalic	$C(OH)_2(CO.OH)_2$	A uric acid derivative. By deoxidation it forms tartronic and afterwards malonic acid.
Tartaric .. .. (dioxysuccinic).	$C_2H_2(OH)_2(CO.OH)_2$	*See* below.
Dioxyadipic ..	$C_4H_6(OH)_2(CO.OH)_2$	
Dioxysuberic ..	$C_6H_{10}(OH)_2(CO.OH)_2$	

Tartaric Acid, $C_2H_2(OH)_2(CO.OH)_2 = C_4H_6O_6$.—*Molecular Weight,* 150.

Natural History.—Ordinary tartaric acid constitutes the acid of grapes, and, together with citric, oxalic, and malic acids, is found in numerous plants.

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Commercial Preparation.—(α.) *Argol* or *tartar* (*hydric potassic tartrate*, $KHC_4H_4O_6$), a substance deposited from fermenting grape juice, is first purified by solution in hot water, and subsequent crystallization (cream of tartar).

(β.) This purified residue is now dissolved in hot water and boiled with powdered chalk, whereby an *insoluble* calcic tartrate, and a *soluble* potassic tartrate are formed:

$$2KHC_4H_4O_6 + CaCO_3 = K_2C_4H_4O_6 + Ca''C_4H_4O_6 + H_2O + CO_2.$$

Hydric potassic tartrate + Calcic carbonate = Potassic tartrate + Calcic tartrate. + Water + Carbonic anhydride.

(γ.) Calcic chloride is now added to the clear solution, whereby the whole of the tartaric acid is precipitated as calcic tartrate: thus,

$$K_2C_4H_4O_6 + Ca''Cl_2 = 2KCl + Ca''C_4H_4O_6.$$

Potassic tartrate + Calcic chloride = Potassic chloride + Calcic tartrate.

(δ.) This tartrate of lime is now collected and boiled with dilute sulphuric acid, whereby an insoluble calcic sulphate is formed, whilst the filtered solution contains the free tartaric acid:

$$Ca''C_4H_4O_6 + H_2SO_4 = C_4H_6O_6 + Ca''SO_4.$$

Calcic tartrate + Sulphuric acid = Tartaric acid + Calcic sulphate.

Tartaric acid may also be prepared by the action of nitric acid on gum or sugar of milk.

Varieties.—There are four modifications of tartaric acid;—

(α.) *Dextro-* or *common tartaric acid*, so called from its property of causing the plane of polarization to rotate to the right.

(β.) *Lævo-tartaric acid*, which rotates the plane of polarization to the left.

(γ.) *Inactive* or *meso-tartaric acid*, which is without action on a polarized ray. It, moreover, cannot be resolved into dextro- and lævo-tartaric acids. In this latter respect it differs from *paratartaric* or *racemic acid*, which is also without action on a polarized ray, but which is a compound of dextro- and lævo-tartaric acid, and is capable of resolution into these two modifications of the acid.

(δ.) *Metatartaric acid.* An uncrystallizable modification produced by fusing the ordinary acid.

Properties of common tartaric acid.—(α.) *Physical.* Colorless crystals (oblique rhombs), inodorous, having an acid taste, permanent in the air, and very soluble in water and alcohol. The crystals fuse at 340° F. (171·1° C.), forming metatartaric and isotartaric acids, both of which are uncrystallizable acids. At 374° F. (190° C.) it loses water, and becomes tartaric anhydride ($C_8H_8O_{10}$), which, by long

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boiling in water, may be converted into tartaric acid. At a temperature of 401° F. (205° C.) it forms paratartaric acid and CO_2.

(*β.*) *Chemical.*—Its solution is very acid, and rapidly decomposes by keeping, acetic acid being formed and a fungus deposited which contains 3·5 per cent. of nitrogen.

With *Hydriodic acid*, it forms succinic and malic acids; with *powerful oxidizing agents*, it forms formic acid; with *mild oxidizing agents*, tartronic acid; fused with *potassic hydrate*, it yields potassic oxalate and acetate, but no hydrogen is evolved; with concentrated *sulphuric acid*, it is carbonized; with *phosphorus pentachloride*, it forms chloromaleic chloride; with *acetic chloride*, it forms diaceto-tartaric acid, $C_2H_2(OC_2H_3O)_2(COOH)_2$; and with *alcohols*, it forms the various ethereal salts.

The following represent the formulas of some of the tartrates :—

Names.	Formula.	Solubility in water.
Potassic tartrates { neutral ..	$K_2C_4H_4O_6$	Very soluble.
Potassic tartrates { acid (Cream of tartar) ..	$KHC_4H_4O_6$	Soluble in boiling but not in cold water.
Ammonic tartrates { neutral ..	$(NH_4)_2C_4H_4O_6$+aq.	Soluble.
Ammonic tartrates { acid ..	$(NH_4)HC_4H_4O_6$	Do.
Sodic tartrates .. { neutral ..	$Na_2C_4H_4O_6$+2 aq.	Do.
Sodic tartrates .. { acid ..	$NaHC_4H_4O_6$+aq.	Do.
Rochelle salt or Seignette salt } Potassic and sodic tartrate	$KNaC_4H_4O_6$+4 aq.	1 in 1½ at 60° F. (15·5° C.)
Potassio-antimonious tartrate, or tartar emetic	$K(SbO)C_4H_4O_6$+aq. heated to 400° F. becomes $KSbC_4H_2O_6$.	1 in 15 at 60° F. (15·5° C.) 1 in 3 at 212° F. (100° C.)

Racemic Acid has the same composition as tartaric acid. It yields the same products as tartaric acid by heat, and forms analogous salts. It differs, however, from tartaric acid in being less soluble in water, and in its solution neither rotating the plane of polarization, nor precipitating a neutral calcic salt.

Fumaric Series.

SERIES II.—*Formula* $C_nH_{2n-2}(CO.OH)_2$.

These dibasic acids form succinic acid with nascent hydrogen, and substitution derivatives of succinic acid with the haloid acids and with the halogens. They also form monochlorinated acids of the malic series with hypochlorous acid.

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The series includes the following:—

ACID.	Formula.	Melting Pt. ° F.	Melting Pt. ° C.	Remarks.
		About		
Fumaric ..	$C_2H_2(COOH)_2$	392·0	200·0	The acid of the common fumitory. Prepared, together with maleic acid, by the action of heat on malic acid. It is a crystalline insoluble acid (1 in 200 at 60° F.). By heat it forms maleic anhydride. With nascent hydrogen it forms succinic acid.
Maleic	Do.	266·0	130·0	See above for preparation. A crystalline volatile soluble acid. Its reactions are similar to those of fumaric acid.
Citraconic ..	$C_3H_4(COOH)_2$	176·0	80·0	Prepared from citric acid. *Citraconic acid* is formed by the prolonged action of heat on citric acid. It is very soluble in water. *Itaconic acid* results when citraconic acid is heated with water for some hours. It is not very soluble in water. *Mesaconic acid* is formed by decomposing the product of the action of heat on a mixture of citraconic and hydrochloric acids. With nascent hydrogen all three yield pyrotartaric acid. The three acids when treated with bromine yield three isomeric brominated acids.
Itaconic ..		320·0	160·0	
Mesaconic ..		392·9	200·5	

Phthalic Series.

SERIES III.—*Formula* $C_nH_{2n-8}(CO.OH)_2$.

These include—

ACID.	Formula.	Melting Point. ° F.	Melting Point. ° C.	
Phthalic ..	$C_6H_4(CO.OH)_2$	365·0	185	By oxidizing benzene and formic acid by MnO_2 and H_2SO_4.
Isophthalic ..		Above 572	Above 300	
Terephthalic		Do.	Do.	
Mesidic ..	$C_6H_3(CH_3)(CO.OH)_2$	550·4	288	
Xylidic ..		541·4	283	
Isoxylidic ..		707·0	375	
Cumidic ..	$C_6H_2(CH_3)_2(CO.OH)_2$	Sublimes.		

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C.—TRIBASIC ACIDS,
and Acids of Higher Basicity, etc.

Tricarballylic Series.

SERIES I.—*Formula* $C_nH_{2n-1}(CO.OH)_3$.

Tricarballylic Acid, $C_3H_5(CO.OH)_3=C_6H_8O_6$ is a trihydric acid, and is produced by heating citric acid with hydriodic acid—

$C_6H_8O_7$	+	2HI	=	$C_6H_8O_6$	+	H_2O	+	I_2.
Citric acid	+	Hydriodic acid	=	Tricarballylic acid.	+	Water	+	Iodine.

Citric Acid (*oxytricarballylic acid*) $C_3H_4(OH)(COOH)_3=C_6H_8O_7$.

Natural History.—This acid is found in the juice of lemons and oranges, and also in many fruits, such as gooseberries, etc., in conjunction with malic acid.

Preparation.—The lemon juice is first allowed to ferment, so that mucilage and other impurities may be separated. The clear liquor is then neutralized with chalk, whereby an insoluble calcic citrate ($Ca_32C_6H_5O_7$) is formed. The precipitate is collected and decomposed with dilute sulphuric acid, the citric acid being afterwards crystallized from the solution.

Properties.—(*α.*) A crystalline dimorphous body, freely soluble in hot and cold water. The crystals fuse at 212° F. (100° C.), and decompose at 300° F. (149° C.), forming aconitic acid. Heated to 338° F. (170° C.), it forms itaconic acid.

(*β.*) *Chemical.*—A tribasic tetrahydric acid. The solution reddens litmus and rapidly decomposes.

It ferments *with putrid flesh,* forming butyric and succinic acids; *sulphuric acid* decomposes it; *nitric acid* converts it into oxalic acid. With *potassic hydrate,* it forms acetic and oxalic acids.

Citric, like tartaric acid, prevents the precipitation of ferric oxide by ammonia. The soluble compound formed has not been very well made out.

The acid is used in medicine, in dyeing, and in calico printing.

Desoxalic or **Trioxycarballylic Acid,** $(C_3H_2(OH)_3(COOH)_3=C_6H_8O_9$, is an unstable acid, and forms, when heated, tartaric and glyoxylic acids.

Meconic Acid ($C_7H_4O_7$) is a tribasic acid present in opium, and consists of mica-like plates, soluble in alcohol and in boiling water, but insoluble in cold water.

Mellitic Acid $C_6(CO.OH)_6$ is a hexabasic acid, existing as an aluminic salt in "*honey stone.*"

We may note that, with one exception, the whole of the benzene (C_6H_6) series of acids, derived by the substitution of the group COOH for the hydrogen of the benzene, are known. Thus—

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Benzoic acid	C_6H_5COOH.
Phthalic acid, etc.	$C_6H_4(COOH)_2$.
Trimellitic acid, etc.	$C_6H_3(CO.OH)_3$.
Pyromellitic acid, etc.	$C_6H_2(COOH)_4$.
Unknown	$C_6H(CO.OH)_5$.
Mellitic acid	$C_6(COOH)_6$.

REACTIONS OF SOME OF THE CHIEF ACIDS.

(I.) Group reactions. (II.) Special reactions.

I.—Group Reactions.

1. Heat the acid in a test tube—

Blackens instantly.	Fuses and blackens after a short time.	Forms a white sublimate, the residue blackening.	Not blackened. White sublimate.	Not blackened. Volatile.
Tartaric (caramel odor). Uric (burnt feather odor). Hippuric (benzene odor). Gallic. Tannic.	Citric.	Malic. Meconic. Pyrogallic.	Oxalic.	Acetic (yields acetone). Formic. Benzoic. Succinic. Butyric. Hydrocyanic. Phenic.

2. Heat the acid in a test tube with sulphuric acid—

Blackens instantly.	Blackens after a time.	Not blackened.	Volatile.
Tartaric. Pyrogallic. Gallic (red). Tannic (brown). Hippuric.	Citric. Malic. Uric. Meconic.	Oxalic. Evolves CO_2 and CO. Sulphocyanic. Evolves CSO, giving odor of SO_2. Hydrocyanic and other cyanogen acids. Evolve CO and NH_3.	Acetic, Formic, Benzoic, Succinic } Evolve CO.

3. Render the acid solution neutral, and add calcic chloride. Filter off the precipitate—

Precipitate. { If soluble in acetic acid = Tartaric acid.
If insoluble in acetic, but soluble in HCl = Oxalic acid.

Filtrate. { Boil with lime water; a precipitate indicates citric acid.
Boil for a long time with lime water and alcohol; a precipitate indicates malic acid.

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4. Add to the acid solution ferric chloride—

A Red Coloration, but no ppt.	Other Reactions.
Acetic; color disappears with HCl	Carbolic; purple.
Formic; ,, ,,	Gallic and tannic; black.
Pyrogallic; ,, ,,	Ferrocyanic; blue.
Sulphocyanic; color disappears with $HgCl_2$, but not with HCl.	Ferricyanic; brown (blue with $FeSO_4$).
Meconic; color neither discharged by $HgCl_2$ nor by HCl.	Benzoic, Succinic, Hippuric } light red.

5. Add to the neutral solution argentic nitrate.

White precipitates occur with the following acids, all of which are soluble in ammonia; viz.: hydrocyanic (insol. in HNO_3; sol. in KCy); sulpho-, ferro-, and ferri-cyanic; meconic; oxalic; succinic; benzoic; tartaric (*see* Tests); citric; malic; acetic. The silver salt is reduced by formic and pyrogallic acids.

6. Add to two portions of the solution, potassic hydrate and hydrochloric acid respectively—

Potassic Hydrate.	Hydrochloric Acid (to neutral solution).
Tartaric; white ppt. on addition of acetic acid.	Uric; white ppt. (powder).
Gallic; green ppt.	Benzoic; ,, (flakes).
Tannic; brown ppt.	Hippuric; ,, (feathery-crystals, soluble in boiling water).
Pyrogallic; black ppt.	

II.—Special Reactions.

Acetic Acid ($C_2H_4O_2$) and the **Acetates.**

1. The acid is soluble in all proportions in water, alcohol, and ether. It dissolves camphor and several resins.

2. *Heat.* The acid and its salts are decomposed, yielding acetone (C_3H_6O).

3. When a mixture of sodic acetate and soda lime is heated, it yields methane or marsh gas ($3NaC_2H_3O_2 + NaHOCa''H_2O_2$ (soda lime) $= 2Na_2CO_3 + CaCO_3 + 3CH_4$).

4. The acetates, heated with alcohol and sulphuric acid, yield the fragrant ethylic acetate ($C_2H_5.C_2H_3O_2$) (*characteristic*).

5. The solid salts, heated with sulphuric acid, yield acetic acid.

6. *Ferric chloride* gives on boiling a deep red coloration, with the precipitation of a basic ferric acetate.

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Oxalic Acid ($C_2H_2O_4$).

1. *Heat;* (α) fuses; (β) gives a white sublimate if carefully heated; (γ) produces dense white fumes towards the end of the reaction, *but never blackens.* (The oxalates of the alkalies and alkaline earths, when heated, leave carbonates, which effervesce with acids; but the oxalates of other metals leave metallic oxides.)

2. H_2SO_4 *and heat;* CO and CO_2 are evolved, but without blackening. (The reaction with the oxalates is similar, a residue of sulphate remaining.)

3. *Calcic chloride* ($Ca''Cl_2$) gives (α) *in very dilute solutions* a ppt., after a time, of calcic oxalate, $Ca''C_2O_4$; (β) in *moderately strong solutions,* it gives an immediate ppt. The ppt. is soluble in HCl or HNO_3 (but not in acetic acid, as in the case of phosphates) and is reprecipitated by ammonia.

The reaction is not interfered with by the presence of ammoniacal salts.

4. *Argentic nitrate* gives a white ppt., $Ag_2C_2O_4$.

Uric Acid ($C_5N_4H_4O_3$).

1. *Heat;* (α) blackens immediately; (β) odor of burnt hair.

2. A drop of *nitric acid,* mixed with uric acid in a capsule, and evaporated to dryness, yields, when the cold residue is touched with ammonia, the deep red tint of murexide ($C_8N_6H_8O_6$).

Hippuric Acid ($C_6H_9NO_3$).—*Crystals;* rhombic prisms, and acicular crystals.

1. *Heat.* (α.) Fuses directly, and volatilizes with partial decomposition, yielding benzoic acid, ammonic benzoate, and benzo-nitrile. (β.) A carbonaceous residue left; any sublimate formed is of a red tint. (γ.) Odor of benzo-nitrile.

[N.B. Hippuric acid is insoluble in ether, but benzoic acid is soluble.]

The hippurates, when fused with excess of potassic hydrate, give off ammonia, and yield benzene by distillation.

Citric Acid ($C_6H_8O_7$).—1. *Heat,* (α) does not blacken immediately; (β) evolves pungent acid fumes; (γ) blackens ultimately (distinguishes it from malic acid).

2. *Sulphuric acid and heat* blackens the acid, but not immediately (distinguishes it from tartaric acid).

3. *Calcic chloride* gives no ppt. on boiling in a solution of the free acid, but on neutralizing the solution with KHO a white insoluble ppt. of calcic citrate is thrown down. The ppt. is insoluble in KHO (distinguishing it from calcic tartrate), but is soluble in NH_4Cl. Boil the ammonic chloride solution, when a white ppt. is thrown down, which is no longer soluble in NH_4Cl.

4. *Calcic citrate* heated with ammonia and argentic nitrate, yields no metallic mirror, thus distinguishing it from tartaric acid.

Malic Acid ($C_4H_6O_5$).—*Crystals;* colorless prisms.

1. *Heat* chars the acid, and yields fumaric acid.

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2. *Calcic chloride;* no ppt. in very dilute aqueous solutions, but a ppt. forms when alcohol is added (calcic malate).

3. *Plumbic acetate,* in neutral solutions a white ppt. (plumbic malate), *sparingly soluble in ammonia,* distinguishing it from plumbic citrate and tartrate, which dissolve easily.

Tartaric Acid ($C_4H_6O_6$).

1. *Heat* (α) blackens immediately; (β) caramel odor; (γ) gives no sublimate.

2. H_2SO_4 *and heat;* (α) blackens immediately; (β) caramel odor. (Reaction similar with tartrates.)

3. *Potassic* (*chloride* or) *acetate* gives a precipitate (with moderately strong solutions) of acid potassic tartrate, $KHC_4H_4O_6$. The delicacy of this reaction is increased—(α) by shaking; (β) by the addition of alcohol.

4. *Calcic chloride* (*in excess*) gives, in moderately strong solutions, an immediate white precipitate of calcic tartrate, $Ca''C_4H_4O_6$, which rapidly becomes crystalline. The precipitate is soluble in KHO or NaHO. Ammoniacal salts prevent the reaction.

Filter off the precipitate and dry gently. Place it in a test-tube with a drop of ammonia and a crystal of argentic nitrate, and heat very gently, when a brilliant silver mirror will be obtained. (This distinguishes it from citric acid.)

5. *Lime and baryta waters, and plumbic acetate;* white precipitates, soluble in excess of acid.

6. *In neutral solutions of tartrates:—*

Argentic nitrate; a white precipitate, soluble in ammonia.

Calcic chloride; a white precipitate.

N.B.—Tartaric acid interferes with the precipitation of ferric hydrate by ammonia, owing to the solubility of the hydrate in a tartaric acid solution.

Benzoic Acid ($C_7H_6O_2$), *Crystals,* prismatic needles.

1. *Heat,* (α) *in a test-tube;* melts at 212° F. (100° C.), and a little above this sublimes; emits an aromatic odor; (β) On *platinum foil;* burns with a smoky flame.

2. *Sulphuric acid* and *heat* does not blacken, but dissolves the acid.

3. *Nitric acid;* no action.

4. Distilled with excess of CaO, yields benzene—($C_7H_6O_2 + CaO = C_6H_6 + CaCO_3$).

5. *Ferric chloride*; a pale, yellow-brown precipitate of basic ferric benzoate ($Bz_6Fe_2O^{vi},Fe_2O_3 + 15$ aq.).

Succinic Acid ($C_4H_6O_4$); *Crystals;* oblique, rhombic prisms.

1. *Heat;* (α) *in test tube*; melts at 356° F. (180° C.), and sublimes in silky needles, emitting an irritating odor; (β) *On platinum foil:* burns with a blue flame, without smoke.

2. *Ferric chloride* gives, in neutral solutions, a brownish-red precipitate of basic ferric succinate, $Sn_3Fe_2O^{vi},Fe_2O_3$, soluble in mineral acids; darkened by ammonia.

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3. *Nitric acid*, no action.

Note the distinctions between benzoic and succinic acids, as follows :—

1. Benzoic acid heated on platinum foil burns with a smoky flame, which succinic acid does not.

2. *Ferric chloride* gives a brown precipitate with both acids. Treat this with ammonia. One portion is decomposed whilst another forms a soluble succinate and benzoate. Filter, and add alcohol and baric chloride to the clear filtrate :—

(α.) With a *ferric succinnate*, a white crystalline precipitate is formed.

(β.) With a *ferric benzoate*, no precipitate is formed.

Tannic Acid—

1. *Heated in tube*, fuses, blackens immediately, and gives no sublimate.

2. *Sulphuric acid and heat;* turns dark brown. (*See* Gallic Acid, which turns red.)

3. *Nitric acid and heat*, a yellow solution, turning red on boiling.

4. *Ferric chloride*, a black precipitate and coloration.

Gallic Acid—

1. *Heated in tube*, fuses, blackens immediately, giving an orange-red sublimate.

2. *Sulphuric acid and heat;* turns magenta red, becoming more intense as the heat increases. (*See* Tannic Acid, which turns brown.)

3. *Nitric acid and heat;* same as Tannic Acid.

4. *Ferric Chloride;* same as Tannic Acid.

Hydrocyanic Acid (*See* page 522).

Ferrocyanic Acid (*See* page 523) ($H_4Fe''Cy_6$).

1. Reaction acid; decomposes alkaline carbonates; stable.

2. *Ferrous sulphate;* a light blue ppt., $K_2Fe.FeCy_6$.

3. *Ferric chloride;* a deep blue ppt. (prussian blue) $'Fe'''_4Fe''_3Cy_{18}$.

Ferricyanic Acid (*See* page 524) ($H_3Fe'''Cy_6$).

1. An unstable acid.

2. *Ferrous sulphate;* a deep blue ppt. (Turnbull's blue) $Fe''_3Fe'''_2Cy_{12}$.

3. *Ferric chloride;* a deep brown coloration.

Sulphocyanic Acid (*See* page 524) (HCNS).

1. Reaction acid; easily decomposed.

2. *Ferric chloride;* a blood-red coloration, but no ppt., even on boiling; *color discharged by mercuric chloride* ($HgCl_2$).

Meconic Acid ($C_7H_4O_7$).

1. *Ferric chloride;* a blood-red coloration; *color not discharged by mercuric chloride.*

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SUPPLEMENTARY CHAPTER.

SUPPLEMENT TO THE FATTY ACIDS (page 605).

Fats and Oils.

Definition.—The fats and oils are combustible bodies, having an unctuous feel, communicating a greasy stain to paper, insoluble in water, but soluble in alcohol and in ether. They are all compounds of glycerine with palmitic, oleic, or stearic acid.

Natural History.—They are found in all parts of the vegetable, but chiefly in the seeds (rape) and fruit (olive.) They also occur in the animal, formed by the conversion of starch and saccharine matters, and are found located chiefly under the cuticle, or in the omentum or round the kidneys. The fat is generally lodged in cells, the envelope of which consists of cellulin or gelatinous tissue. Fat not unfrequently occurs as a product of tissue degeneration (as in the kidney, liver, etc.), and is also found as a product of secretion (as in milk).

Preparation.—(1.) *By simple pressure* (croton, olive, almond, linseed, mustard, etc.).

(2.) *By heat and pressure,* as in the case of the solid fats (such as lard, human, cod-liver (dark colored), castor (hot drawn), etc.

(3.) *By cold and pressure* (castor and cod-liver (cold drawn), lard).

(4.) *By distillation* (volatile oils); (*see* page 551).

(5.) *By destructive distillation* (coal-tar oils).

(6.) *By solution in a fixed oil, in alcohol, or in ether* (yelk oil).

(7.) *By fermentation* (oil of bitter almonds).

CLASSIFICATION.

I. *Fixed oils;* that is, oils which decompose at a temperature below that at which they distil, and impart a *permanently* greasy stain to paper.

II. *Volatile oils;* that is, oils which may be distilled unchanged, and that impart a greasy stain to paper, which is not permanent.

I.—Fixed Oils.

The fixed oils are composed of two or more neutral substances,

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combined with some of the acids of the acetic series, or with acids closely allied to them.

These are divided into two classes:—

(A.) *Saponifiable oils.*

(B.) *Non-saponifiable oils.*

(A.) **Saponifiable Fixed Oils.**—Some of these are *solid*, as, *e.g.*, palm oil; and some are *liquid*, as, *e.g.*, olive oil. Of animal fats, those from *warm*-blooded animals are usually solid at ordinary temperatures (such as suet); whilst those from *cold*-blooded animals are commonly liquid (such as the fish oils). The fats and oils have very little odor or taste. Their specific gravity varies from 0·91 to 0·94.

The action of heat.—The liquid oils may be solidified by cold. The solid fats melt at from 70° to 140° F. (21·1° to 60° C.). At 500° F. (260° C.) they usually undergo slight decomposition. At about 600° F. (315·5° C.) (that is, below the temperature at which they distil—hence they are termed *fixed oils*), they decompose, giving off carbonic anhydride and acrolein. At a higher temperature, as, *e.g.*, when dropped on a red-hot iron plate, they are decomposed into various hydrocarbons (oil gas).

Solubility.—They are all insoluble in water, but soluble in boiling alcohol and in cold ether. They are solvents of sulphur, phosphorus, etc.

Action of Air.—(*α.*) *Rancidity.* By exposure to air the oils commonly turn rancid. This, however, does not occur in the case of pure oil. Rancidity is brought about by the presence in the oil of certain albuminous matters, which, during decay, decompose the glyceric oleate, or the glyceric salts of other acids.

(*β.*) *Drying and non-drying oils.*—Most fats and oils, when exposed to the air, absorb oxygen (some at the same time evolving carbonic anhydride), ultimately becoming solid. These are called "drying oils," of which linseed, rape, and mustard are illustrations. They contain glyceric oleate (olein), or glyceric salts of acids homologous to oleic acid. This oxidation process has, in some cases, been so rapid that active combustion has resulted. This property of drying is, in many cases, increased by dissolving in the oil when hot a twentieth part of its weight of litharge or oxide of manganese. This constitutes (as in the case of linseed) what is called "boiled oil." Other oils do not absorb oxygen;—chemically, they differ from the drying oils in containing glyceric salts of acids other than those belonging to the oleic series, as linoleic acid, the acid of linseed; nevertheless, they gradually alter by exposure, though in a different manner. These are called "non-drying oils," such as olive, almond, rape-seed oils, etc.

The oils are all decomposed by the action of the haloids.

Acids act on them, forming various compounds.

With the fixed alkalies they form salts called soaps (saponification).

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Potash forms with them soft soap, and soda hard soap. Ammonia does not form true soaps with the oils, but compounds called amides.

The fats combine with metallic oxides and hydrates to form plasters, glycerin being set free. Thus—

$$3PbO + 3H_2O + 2(C_3H_5.3C_{18}H_{33}O_2) = 3(Pb2C_{18}H_{33}O_2) + 2(C_3H_53HO).$$

Plumbic oxide + Water + Oleate of glyceryl (olive oil) = Oleate of lead (lead plaster) + Glycerin.

The following is a tabulated list of the principal fats and oils:—

Name.	Source.	Sp. Gr.	Fusibility. F.	
1. *Non-drying Oils.*				
Olive	Olea europæa..	0·918	Solid below 32° F. (0° C.)	*Virgin oil* is the oil obtained by pressure without heat.
Almond	Amygdalus communis	0·918 at 60° F.	Solid below—13° F. (—25° C.)	Seeds yield 50 per cent. of oil.
Sesamé	Sesamum indicum			
Rapeseed				
Mustard				Yields erucic acid on saponification.
Colza	Brassica oleifera	0·913		
Yelk				
Male fern	Filix mas			Contains filicic acid, $C_{14}H_{18}O_5$.
Human				Contains olein and margarine.
2. *Drying Oils.*				
Linseed	Linum usitatissimum	1·939 at 54° F.	Solid at —15° C.)	25 per cent. extracted from seed; 12 per cent. left in the cake.
Walnut			} Liquid at ordinary temperatures.	
Hempseed ..				
Poppyseed ..				
Croton				Tiglic acid, but not crotonic acid, is obtained from the oil.
Castor	Ricinus communis	0·969	Solid at – 14° F. (—25·6° C.)	A *riconoleate* of glyceryl (C_3H_5 $3C_{18}H_{33}O_3$).
3. *Fish Oils.*				
Sperm	*Liquid* fat in head of spermaceti whale.	0·868	Solid at 45° F. (7·2° C.)	Contains phocenin.
Common whale	Common whale	0·927	Solid at 32° F. (0° C.)	
Cod liver	Gadus morrhua		Solid at 30° F. (—1° C.)	Contains constituents of bile; also a phosphorized fat (the oil gives a crimson with H_2SO_4).
4. *Solid Fats.*				
Tallow	Fat of ox, sheep, etc.			Suet; almost entirely stearine.
Lard	Soft fat of pig			
Butter	Milk			
Palm	Elais guineensis		81° F. (27·2° C.	Becomes more solid by keeping.
Nutmeg butter	Myristica		87° F. (30·5° C.)	Volatile oil and myristin (C_3H_5 $3C_{14}H_{27}O_2$).
Cocoa nut.. ..	Cocos nucifera		68° F. (20° C.)	Contains glycerin, combined with caproic, caprylic, lauric, myristic, and palmitic acids. Used for marine soap, being soluble in NaCl.
Cacao butter ..	Theobroma cacoa		85° F. (29·5° C.)	Chiefly stearine.
Laurel fat.. ..				
Yellow wax ..	Honeycomb of bee	0·96	145° F. (63° C.)	White wax is the yellow wax bleached. Contains cerblein (5 per cent.) and cerotic acid.
Spermaceti ..	*Solid* fat in head of spermaceti whale	0·940	120° (49° C.)	Palmitate of cetyl yields ethal (not glycerine) on saponification.

The following Table, from Bloxam, shows the principal fatty bodies, and their corresponding acids and fusing points.

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Neutral Fats.	Formula.	Chief Source.	Fusing Point. ° F.	Fatty Acids.	Formula.	Fusing Point. ° F.
Stearin ..	$C_{57}H_{110}O_6$	Tallow.	125 to 157	Stearic.	$C_{18}H_{36}O_2$	159
Palmitin ..	$C_{51}H_{98}O_6$	Palm oil.	114 to 145	Palmitic.	$C_{16}H_{32}O_2$	144
Margarin ..	$C_{54}H_{104}O_6$	Olive oil.	116	Margaric.	$C_{17}H_{34}O_2$	140
Olein ..	$C_{57}H_{104}O_6$	Do.	Below 32	Oleic.	$C_{18}H_{34}O_2$	40
Cetin ..	$C_{32}H_{64}O_2$	Spermaceti.	120	Palmitic.	$C_{16}H_{32}O_2$	144
Myricin ..	$C_{46}H_{92}O_2$	Bees'-wax.	162	Do.		

(B.) **Nonsaponifiable Fats.**—This includes certain bodies, such as cetene and ethal from spermaceti, myricin and ceren from bees'-wax, cholesterin, etc.

They are all solid crystalline bodies, and fuse at temperatures varying from 180° to 300° F. (82° to 149° C.).

II.—Volatile Oils. (*See* page 551.)

Soaps.

A soap results from the action of alkalies on fats and oils. If potash be used for effecting saponification, a hard soap results; if soda, a soft soap. Tallow, palm-oil, cocoa-nut oil, and kitchen stuff are the fats commonly employed in the manufacture of hard soap, whilst seal and whale oil are used for soft soap. We may here note that—

(α.) *Tallow* consists of about three parts of solid stearin (or the glyceride of stearic acid), and one part of liquid olein (or the glyceride of oleic acid).

(β.) *Palm oil* consists chiefly of solid palmitin (or the glyceride of palmitic acid) and olein.

(γ.) *Seal and whale* oils consist chiefly of olein.

I. *Hard soaps.*—The fat is first boiled in a soda ley. When perfectly dissolved a quantity of common salt is added (*salting out*). The soap immediately rises to the surface, being insoluble in a solution of common salt. Thus an insoluble sodic stearate (or, if palm-oil be used, sodic palmitate) and sodic oleate are formed, whilst the glycerin remains in solution. Thus—

(α.) $C_3H_5(C_{18}H_{35}O)_3.O_3 + 3NaHO = 3(C_{18}H_{35}O(NaO)) + C_3H_8O_3.$

Stearin; or glyceride of stearic acid + Caustic soda = Sodic stearate + Glycerin.

(β.) $C_3H_5(C_{18}H_{33}O)_3.O_3 + 3NaHO = 3(C_{18}H_{33}O(NaO)) + C_3H_8O_3.$

Olein; or glyceride of oleic acid + Caustic soda = Sodic oleate + Glycerin.

The soap, that is, the sodic stearate and oleate, is then allowed to collect on the surface, whilst the alkaline ley containing the glycerine is drawn off from below. The soap is then pressed in iron moulds.

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If *tallow* has been used, the soap is a mixture of *stearate* and oleate of soda; but, if *palm oil*, of *palmitate* and oleate of soda.

Transparent soaps are prepared by first drying the soap, then dissolving it in spirits of wine by heat, and pouring the solution into moulds after a sufficient quantity of spirit has been removed by distillation, so that the solution may set perfectly when cold.

Glycerine soap consists of a mixture of the soap and the alkaline solution containing the glycerin, as small a quantity of water being used in the operation as possible.

In *silicated soap*, silicate of soda is mixed with the soap.

In the *common yellow soaps*, a quantity of common rosin is used.

Castile soap is made from olive oil, which contains the glycerides both of palmitic and stearic acids (margarine), as well as oleic acid. Hence Castile soap is a mixed stearate, palmitate and oleate of soda.

The appearance of *mottled soap* depends on the presence of veins of oxide of iron. It is supposed to indicate that the soap is tolerably free from water.

II. *Soft soaps.*—In fish oil, which is the fat used for soft soaps, olein, or the glyceride of oleic acid, predominates. This, with a *potash ley*, yields *oleate of potash*, of which soft soaps are principally composed. The separation of the soft soap is not effected by salting, but the solution is simply evaporated to the necessary consistency. If common salt was used, the soft soap would then be converted into a hard soda soap.

Candles.

Stearic acid is commonly employed in preference to tallow for candles, because it fuses at a much higher temperature 159° F. (70·5° C.).

I. *The old process of Saponification by Lime.*—The melted tallow is first mixed with lime and water, and the mixture subjected to the action of superheated steam. In this way an insoluble stearate and oleate of lime are formed. These are then separated from the solution which contains the glycerin, and are decomposed by the action of sulphuric acid. The mixed stearic and oleic acids set free, are submitted to pressure in a hydraulic press, whereby the oleic acid is squeezed out, and stearic acid, mixed with more or less palmitic acid, obtained.

II. *The process called Saponification by Sulphuric Acid.*—The fats (palm oil, cocoa-nut oil, or any kind of refuse fat), are first mixed in copper boilers with about one-sixth their weight of sulphuric acid, and the mixture heated by steam for some time to 350° F. (176·1° C.). The sulphuric acid converts a part of the glycerin into sulpho-glyceric acid ($C_3H_8O_3.SO_3$), and decomposes the remainder, a mixture of crude palmitic, stearic and oleic acids remaining (probably as sulpho-acids),

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together with a solid, fatty acid, called *elaidic acid*, isomeric with, and derived from the liquid oleic acid. Thus it will be noted that the quantity of solid fats obtained by this process is increased. These fatty acids, after being collected and well washed, are distilled in a current of steam heated to 600° F. (315·5° C.), the oleic acid being removed from the distillate by pressure. A pitchy matter remains in the retort, which is used in the manufacture of black sealing-wax.

III. *Saponification (so called) by Steam.*—The advantage of this process is that the glycerin can be obtained at once in a pure state. It consists in merely distilling the fat by the action of superheated steam at 600° F. (315·5° C.), when both glycerin and fatty acids distil over. After the distillate has stood for a short time, the fatty acids collect on the surface of the glycerin, and on removal may be at once subjected to pressure to separate the oleic acid. The glycerin, as obtained by this process, is fit for the market.

The Tannins.

The Tannins are a class of amorphous bodies, widely distributed, constituting the astringent principles of plants. Our knowledge of these bodies, which are probably modifications of tannic acid, is very limited. The following special reactions are to be noted:—

1. They have all a slightly acid reaction, and a very astringent taste.
2. They yield a blue-black, and in some cases a green precipitate, with ferric salts.
3. They precipitate albumen and gelatine from their solutions.
4. They form leather (a substance having a power of resisting putrefaction) with animal membranes. [NOTE.—Gallic acid has no such power.]

The tannic acid of the oak, (*gallotannic acid*; $C_{27}H_{22}O_{17}$), or, what is more probably a glucoside of tannic acid, is extracted by a mixture of water and ether from certain growths called "nut-galls," occurring on the leaves of the *Quercus infectoria*, and said to be produced by the puncture of an insect.

Tannic acid is a yellowish amorphous mass, resolved by heat into carbonic anhydride, pyrogallic and metagallic acids. It is soluble in water, the solution reddening litmus. When boiled with acids or with a strong solution of potash, it splits up into glucose and gallic acid, the same change occurring spontaneously when the powdered galls, mixed with water, are allowed to ferment. This fermentative process results from the presence in the nut-galls of a nitrogenized body, capable of acting as a ferment. The glucose formed ultimately undergoes alcoholic fermentation.

The tannins that turn ferric salts *black*, yield *pyrogallol* ($C_6H_6O_3$) on dry distillation; whilst those that turn ferric salts *green*, yield *pyrocatechin* ($C_6H_6O_2$).

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Ink.—This consists of a mixture of nut-galls with water, gum, and ferrous sulphate. By standing, the ferrous salt is converted into a ferric salt, and a black tannate of ferric oxide (?) formed. A trace of creosote is usually added, to prevent the ink becoming mouldy. The brown colour of old ink is due to the oxidation of the tannic acid, leaving simply the brown ferric oxide. Ink leaves an iron-mould stain wherever it has fallen on linen after the fabric has been washed, from the removal of the tannic acid by the alkali of the soap.

Tanning.—The skin (that is to say, the dermis or true skin) is converted into leather by the action of tannic acid on the gelatine. The leather formed is tough, resists putrefaction, and is impermeable to water.

(α.) The skin is first soaked in lime-water for the purpose of saponifying the fat, and dissolving the sheath of the hairs, so that their removal may be easily effected.

(β.) After the skin has been cleansed and the hair removed, it is placed in very dilute sulphuric acid, in order that any adherent lime may be neutralized (otherwise a tannate of lime would be afterwards formed), and also to "raise the skin," that is, to open the pores to receive the tanning liquid.

(γ.) The skin is then placed in an infusion of oak-bark (*ooze*) for a few weeks, and, finally, a number of skins are arranged in layers in a pit, coarse ground oak-bark being placed between each skin. Sometimes sumach (the ground shoots of the *rhus coriaria*) is used in the place of oak-bark. On removal from the pit, the skins are dried in a free current of air.

Currying consists in wetting the leather first with water, and afterwards with oil. As the water evaporates the oil sinks into the skin.

In *tawing* (as in the preparation of kid for gloves), the lime on the skin is removed by lactic acid (a sour mixture of bran and water being commonly employed). The skin is afterwards impregnated with aluminic chloride (a bath of alum and salt being commonly used), which effectually prevents putrefaction.

In *shamoying* (as in the preparation of wash-leather), the skin is first sprinkled with oil, and then beaten with wooden hammers. It is afterwards exposed to a warm atmosphere in order to dry the oil, any excess of oil being removed by a weak alkaline bath.

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CHAPTER XXV.

THE ETHERS.

OXY-ETHERS—Ethers of Monohydric Alcohols—Preparation—Ethers of Di- and Trihydric Alcohols. SULPHO-ETHERS. HALOID ETHERS.

I. Oxy-Ethers.

These ethers are the oxides of alcohol radicals. The relationship subsisting between a *metallic hydrate*, as NaOH, and a *metallic oxide*, as Na_2O, has its counterpart in the relationship between *an alcohol* (that is, a hydrate of an alcohol radical) as *ethylic alcohol*, $C_2H_5(OH)$, and an *oxy-ether* (that is, an oxide of an alcohol radical) as *ethylic ether*, $(C_2H_5)_2O$.

Just, too, as we have monohydric, dihydric, and trihydric alcohols, so we have ethers of monohydric, dihydric, and trihydric alcohols respectively.

Ethers of Monohydric Alcohols.

ETHERS.	Formula.	Boiling Pt.		Sp. Gr.	Remarks.
		° F.	° C.		
Methylic	$(CH_3)'_2O$	−5·8	−21	1·617	A colorless liquid. Does not liquefy at −16° C. Burns with a feebly luminous flame. The vapor is soluble in water (33 in 1), alcohol, wood spirit, and sulphuric acid. It forms substitution compounds with Cl, as $(CH_2Cl)_2O$, etc.
Methylic ethylic ..	$(CH_3)'(C_2H_5)'O$	51·8	11		
Methylic amylic ..	$(CH_3)(C_5H_{11})O$	197·6	92		
Ethylic (ether) ..	$(C_2H_5)'_2O$	96·0	35·6	0·723	A colorless, very volatile liquid; will not freeze; combustible; vapor density (air=1) 2·586. Explodes when mixed with oxygen. Soluble in water (1 in 10). Miscible in all proportions with alcohol. Forms with H_2SO_4, sulphovinic acid. By oxidation from exposure to air, it forms acetic acid, and by the action of hot nitric acid, carbonic, acetic, and oxalic acids. With chlorine it forms substitution products.
Ethylic butylic ..	$(C_2H_5)(C_4H_9)O$	176·0	80		
Ethylic amylic ..	$(C_2H_5)(C_5H_{11})O$	233·6	112		
Butylic	$(C_4H_9)''_2O$	219·2	104		
Amylic	$(C_5H_{11})'_2O$	348·8	176		
Allylic	$(C_3H_5)'_2O$	179·6	82		
Phenylic	$(C_6H_5)_2O$				
Benzylic..	$(C_7H_7)_2O$				
Phenylbenzylic ..	$(C_6H_5)(C_7H_7)O$				

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Preparation of the Simple and Mixed Ethers (General).

(I.) *In the case of the ethers derived from the alcohols of the methylic series* ($C_nH_{2n+1}OH$), *or of the vinylic series* ($C_nH_{2n-1}OH$).

Preparation.—By the action of sulphuric acid on the alcohol. The process takes place in two stages:—

(*a.*) The sulphuric acid first converts a portion of alcohol into a sulpho-acid.

$C_2H_5(OH)$	+	H_2SO_4	=	$C_2H_5HSO_4$	+	H_2O.
Ethylic alcohol	+	Sulphuric acid	=	Sulpho-ethylic acid (sulphovinic acid)	+	Water.

(*β.*) This sulpho-acid then reacts on a fresh portion of alcohol.

$C_2H_5HSO_4$	+	$C_2H_5(OH)$	=	$(C_2H_5)_2O$	+	H_2SO_4.
Sulpho-ethylic acid	+	Ethylic alcohol	=	Ethylic ether	+	Sulphuric acid.

[NOTE.—A. That the sulphuric acid concerned in the first stage of the reaction is set free in the second stage. Thus, theoretically, a small quantity of acid should convert an unlimited quantity of alcohol into ether.

B. That by boiling the ethers with dilute sulphuric acid they are converted into their corresponding alcohols. Thus :—

(*a.*) $(C_2H_5)_2O + 2H_2SO_4 = 2[(C_2H_5)HSO_4] + H_2O$.

(*β.*) $(C_2H_5)HSO_4 + H_2O = H_2SO_4 + C_2H_5(OH)$.]

(II.) *In the case of ethers derived from the alcohols of the ethylic series* ($C_nH_{2n+1}OH$), *of the vinylic series* ($C_nH_{2n-1}OH$), *and of the benzylic series* ($C_nH_{2n-7}OH$).

Preparation.—By the action of an iodide derivative of the corresponding hydrocarbon on the sodium or potassium derivative of the corresponding alcohol.

Thus, say we wish to prepare ethylic ether :

(*a.*) By the action of sodium on ethylic alcohol, we first form a sodium derivative :—

$2C_2H_5.OH$	+	Na_2	=	$2C_2H_5.NaO$	+	H_2.
Ethylic alcohol	+	Sodium	=	Sodic ethylic alcohol	+	Hydrogen.

(*β.*) By the action of ethylic iodide (C_2H_5I) on the sodic ethylic alcohol, we form ethylic ether and sodic iodide.

$C_2H_5(NaO)$	+	C_2H_5I	=	$(C_2H_5)_2O$	+	NaI.
Sodic ethylic alcohol	+	Ethylic iodide	=	Ethylic ether	+	Sodic iodide.

It will be seen that *a simple ether* is formed when the haloid derivative acts on a metallic derivative of *a corresponding* alcohol, *e.g.*, when *ethylic* iodide acts on sodic *ethylic* alcohol, ethylic ether, $(C_2H_5)O$, is formed; but that a *mixed ether* will be produced when the haloid derivative acts on the metallic derivative of some *isomeric*

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or *homologous* alcohol; *e. g.*, when *ethylic* iodide acts on sodic *methylic* alcohol, methylic ethylic ether $(CH_3)(C_2H_5)O$ is formed.

(III.) Phenylic ether is prepared by fusing together phenol and diazo-benzene sulphate. Thus—

$C_6H_5(N_2HSO_4)$	+	$C_6H_5(OH)$	=	$(C_6H_5)_2O$	+	N_2	+	H_2SO_4.
Diazobenzene sulphate	+	Phenol	=	Phenylic ether	+	Nitrogen	+	Sulphuric acid.

Ethers of Dihydric Alcohols.

Ether.	Formula.	Boiling Point.	
		° F.	° C.
Ethylenic	C_2H_4O	55·4	13·0
Propylenic	C_3H_6O	63·0	35·0
Amylenic	$C_5H_{10}O$	171·0	95·0

Preparation (*general*).—By the action on the glycols (dihydric alcohols) (α), first, of hydrochloric acid, whereby *a chlorhydrin* is formed; and (β), afterwards, by the withdrawal of hydrochloric acid from the chlorhydrin, by the action of potassic hydrate. These two stages are seen in the preparation of ethylenic ether, as follows:—

(α.)	$C_2H_4(OH)_2$	+	HCl	=	$C_2H_4(OH)Cl$	+	H_2O.
	Glycol	+	Hydrochloric acid	=	Ethylenic chlorhydrate	+	Water.

(β.)	$C_2H_4(OH)Cl$	+	KHO	=	C_2H_4O	+	KCl	+	H_2O.
	Ethylenic chlorhydrate	+	Potassic hydrate	=	Ethylenic ether	+	Potassic chloride	+	Water.

Ethylenic Ether; *Ethylenic oxide* (C_2H_4O). *Molecular weight*, 44. *Molecular volume*, [| |]. *Boils at* 56·3° F. (13·5° C.).

Preparation.—(Described above).

This ether is the only one of these ethers that has received much attention.

It combines *with acids* as a base; thus, $C_2H_4O + HCl = C_2H_4(OH)Cl$.

It combines *with water* to form glycol; thus, $C_2H_4O + H_2O = C_2H_4(OH)_2$.

It precipitates many *metallic salts*, as hydrates, from their solutions; thus, $2C_2H_4O + MgCl_2 + 2H_2O = 2[C_2H_4(OH)Cl] + MgH_2O_2$.

With *nascent hydrogen* it forms alcohol; thus, $C_2H_4O + H_2 = C_2H_5(OH)$.

With *oxygen* it forms glycollic acid; thus, $C_2H_4O + O_2 = C_2H_4O_3$.

Ether of the Trihydric Alcohols.

Glycylic Ether, $(C_3H_5)_2O_3$, is the only ether of this class known. It is prepared by heating together glycerin and calcic chloride, the

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calcic chloride abstracting three molecules of water from the glycerin. Thus—

$$2(C_3H_5(OH)_3) = 3H_2O + (C_3H_5)_2O_3.$$
Glycerin = Water + Glycylic ether.

II.—Sulpho- or Thio-Ethers.

These sulpho-ethers bear the same relationship to the mercaptans as the ethers bear to the alcohols. Thus—

$$C_2H_5(OH) - C_2H_5.O.C_2H_5 \; ; \; C_2H_5(SH) - C_2H_5.S.C_2H_5.$$
Alcohol — Ether ; Mercaptan — Sulpho-ether.

Preparation.—(1.) By the distillation of the lead derivatives of the mercaptans $[(C_2H_5S)_2Pb=(C_2H_5)_2S+PbS]$.

(2.) By the action either (α) of potassic or sodic sulphide, or (β) of the sodic or potassic derivatives of the mercaptans, on the monohaloid derivatives of certain hydrocarbons. Thus :—

(α.) $2C_2H_5Br+K_2S=(C_2H_5)_2S+2KBr.$

(β.) $C_2H_5I+C_2H_5(NaS)=NaI+(C_2H_5)_2S.$

III.—Haloid Ethers.

These ethers are alcohols where a haloid element or a cyanogen group has been substituted for a semi-molecule of hydroxyl.

These compounds are formed either by the action on the alcohols (α) of the haloid acids, or (β) of the compounds of phosphorus with the haloids; or (γ) by the direct substitution of the haloids for hydrogen in saturated hydrocarbons. Thus :—

(α.) $C_2H_5(OH)+HCl=C_2H_5Cl+H_2O.$

(β.) $3C_2H_5.OH+PCl_3=3C_2H_5Cl+H_3PO_3.$

(γ.) $CH_4+Cl_2=CH_3Cl+HCl.$

The preparation of the nitriles is described elsewhere.

The composition and properties of the most important of the haloid ethers have been already described under the several hydrocarbons of which they are derivatives.

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CHAPTER XXVI.

THE ALDEHYDES.

(Alcohol Dehydrogenatum).

The Aldehydes—Constitution—Preparation—Reactions—Aldehydes of the Acetic Series—Formic Aldehyde—Aldehydes of the Acrylic and Benzoic Series—Other Aldehydes.

The aldehydes are formed from the alcohols by the simple withdrawal of hydrogen. Thus an aldehyde occupies an intermediate position between an alcohol and an acid, containing, in the case of the aldehydes of monohydric alcohols, two hydrogen atoms less than the corresponding alcohol, and one oxygen atom less than the corresponding acid. Thus—

$CH_3.CH_2OH$;	$CH_3.COH$;	$CH_3.COOH$.
Ethylic alcohol ;	Acetic aldehyde ;	Acetic acid.

There are reasons to believe that the hydrogen of the alcohol displaced to form an aldehyde, is the H_2 of the group CH_2OH. Hence it is customary to represent an aldehyde of a monohydric alcohol by the formula R′COH, and of a dihydric alcohol by the formula $R''(COH)_2$, etc. The aldehydes of monohydric and of dihydric alcohols only are known.

The following are the formulas of the aldehydes of monohydric alcohols :—

Acetic series of aldehydes		$C_nH_{2n+1}COH$.
Acrylic	,,	$C_nH_{2n-1}COH$.
		$C_nH_{2n-5}COH$.
Benzoic	,,	$C_nH_{2n-7}COH$.
		$C_nH_{2n-9}COH$.

Preparation.—(General methods.)

(1.) *From the alcohols;* by oxidation, as, *e.g.*, by atmospheric air; by the action of chlorine on the dilute alcohol; by the action of dilute sulphuric acid and potassic bichromate, etc. Thus—

$C_2H_5(OH)$	+	O	=	CH_3COH	+	H_2O.
Ethylic alcohol	+	Oxygen	=	Acetic aldehyde	+	Water.

(2.) *From the acids;* by the dry distillation of calcic, sodic or potassic formate with the corresponding metallic salt of a monobasic acid. Thus—

$COH(OK)$	+	$CH_3CO(OK)$	=	CH_3COH	+	K_2CO_3.
Potassic formate	+	Potassic acetate	=	Acetic aldehyde	+	Potassic carbonate.

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Reactions.—(1.) *Their conversion into the corresponding alcohols.*—By the action of nascent hydrogen (*e.g.*, by the action of water on sodium amalgam). Thus—

$$\underset{\text{Acetic aldehyde}}{CH_3COH} + \underset{\text{Hydrogen}}{H_2} = \underset{\text{Ethylic alcohol.}}{C_2H_5(OH).}$$

(2.) *Their conversion into the corresponding acids.*—By oxidation (*e.g.*, by the action of air). Thus—

$$\underset{\text{Acetic aldehyde}}{CH_3COH} + \underset{\text{Oxygen}}{O} = \underset{\text{Acetic acid.}}{CH_3COOH.}$$

(3.) *Their conversion into the potassic salts of the corresponding acids.*—By fusion with potassic hydrate. Thus—

$$\underset{\text{Acetic aldehyde}}{CH_3.COH} + \underset{\text{Potassic hydrate}}{KHO} = \underset{\text{Potassic acetate.}}{CH_3CO(OK)} + \underset{\text{Hydrogen.}}{H_2.}$$

(4.) *Their conversion into chloraldehydes* (*i. e.*, Cl_2 being substituted for O).—By the action of phosphoric chloride. Thus—

$$\underset{\text{Acetic aldehyde}}{CH_3(COH)} + \underset{\text{Phosphoric chloride}}{PCl_5} = \underset{\text{Chlor-aldehyde.}}{CH_3(CCl_2H)} + \underset{\text{Phosphoric oxytrichloride.}}{PCl_3O.}$$

(5.) *Their conversion into acid chlorides.*—By the action of chlorine or bromine. Thus—

$$\underset{\text{Acetic aldehyde}}{CH_3(COH)} + \underset{\text{Chlorine}}{Cl_2} = \underset{\text{Hydrochloric acid}}{HCl} + \underset{\text{Acetyl chloride.}}{CH_3(COCl).}$$

The aldehydes form crystalline compounds with the acid sulphites of the alkali metals. The aldehydes of the acetic series form *with ammonia* aldehyde ammonias. They also unite with aniline to form *phenylated aldines*, and with urea to form *ureides*. They also combine with hydrocyanic acid.

Aldehydes of the Acetic Series ($C_nH_{2n+1}COH$).

Name.	Formula.	Fusing Point.		Boiling Point.	
		° F.	° C.	° F.	° C.
Formic aldehyde ..	H,COH				
Acetic „ ..	CH_3,COH			69·8	21
Propionic „ ..	C_2H_5,COH			118·4	48
Butyric „ ..	$C_3H_7(\alpha)$COH			167·0	75
Isobutyric „ ..	$C_3H_7(\beta)$COH			143·6	62
Valeric „ ..	$C_4H_9(\alpha)$COH			217·4	103
Isovaleric „ ..	$C_4H_9(\beta)$COH			199·4	93
Caproic „ ..	$C_5H_{11}(\beta)$COH			249·8	121
Œnanthylic „ ..	$C_6H_{13}(\alpha)$COH	10·4	−12	305·6	152
Cuprylic „ ..	$C_8H_{16}O$			352·4	178
Palmitic „ ..	$C_{16}H_{32}O$	125·6	52		

Formic Aldehyde (*Methylic Aldehyde*) HCOH. A gaseous body.

Preparation.—By the action of an incandescent platinum wire on a mixture of air and the vapor of methylic alcohol.

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Acetic (or **Ethylic**) **Aldehyde** ($CH_3.COH$) (often simply called *aldehyde.*) *Molecular weight*, 44. *Molecular volume* [|]. *Sp. Gr.* 0·805. *Boils at* 69·8° F. (21° C.).

Properties.—A colorless, volatile and very acrid liquid, soluble in water in all proportions, having a neutral reaction, but becoming acid (acetic acid) on exposure to air. So great is its attraction for oxygen that it reduces the salts of silver to the metallic state. Thus by heating a mixture of aldehyde and argentic nitrate with a trace of ammonia in a test tube, the silver is deposited as a brilliant metallic mirror on the sides of the tube. When treated with potassic hydrate, aldehyde is decomposed, and a brown substance formed, called "resin of aldehyde." With hydrochloric acid it forms *aldol* ($C_4H_8O_2$).

There are three isomeric modifications of aldehyde, *viz.*—

Metaldehyde; crystalline; sublimes at 248° F. (120° C.).

Paraldehyde; liquid; boils at 257° F. (125° C.).

Elaldehyde; crystalline; fuses at 35·6° F. (2° C.); boils at 201·2° F. (94° C.).

Chloral, $CCl_3(COH)$.—By the action of chlorine, aldehyde is transformed into the compound called chloral or trichloraldehyde, the H_3 of the CH_3 being replaced by Cl_3. Thus—

$CH_3.COH$;	$CCl_3.COH$.
Acetic aldehyde;	Chloral.

Properties.—Chloral is a colorless liquid (specific gravity 1·5) boiling at 201·2° F. (94° C.). It combines rapidly with water to form *chloral hydrate,* $CCl_3CH(OH)_2$. By oxidation it forms *trichloracetic acid,* $CCl_3CO(OH)$, and by the action of nascent hydrogen it is reduced to aldehyde. By the action of alkalies it is at once decomposed into chloroform and a formate ($CCl_3COH + KHO = CCl_3H + HCO(OK)$).

Acetal.—When gaseous hydrochloric acid is passed into a solution of aldehyde in anhydrous alcohol, a compound of aldehyde and ethylic chloride is formed, which, by heating with sodic ethylate, forms a compound of aldehyde and ethylic oxide called *acetal* ($C_6H_{14}O_2$) = $C_2H_4(OC_2H_5)_2$. Acetal is a colorless liquid; specific gravity 0·821°, boiling at 284° F. (140° C.). Under the action of platinum black it forms, first, aldehyde, and afterwards acetic acid.

Aldehydes of the Acrylic Series ($C_nH_{2n-1}COH$).

Of this series two members are known.

Name.	Formula.	Boiling Point.		
		° F.	° C.	
Acrylic aldehyde (Acrolein).	C_3H_4O	126·5	52·5	A colorless mobile liquid. By oxidation it forms acrylic acid ($C_3H_4O_2$).
Crotonic aldehyde	C_4H_6O	220·1	104·5	

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Aldehydes of the Benzoic Series ($C_nH_{2n-7}COH$).

The following members are known :—

Aldehyde.	Formula.	Boiling Point.		
		° F.	° C.	
Benzoic .. .. (Bitter almond oil; Benzaldehyde).	$C_6H_5(COH)$	356·0	180·0	*Preparation.*—(1.) By the oxidation of amygdalin. (2.) By digesting bitter almonds with water (action of synaptase on amygdalin). *Properties.*—A colorless liquid, Sp. Gr. 1·043. Absorbs oxygen from the air, becoming benzoic acid.
Paratoluic	$C_6H_4(CH_3)(COH)$	399·2	204·0	
Alpha-toluic ..	$C_6H_5CH_2(COH)$			
Cumic	$C_6H_4(C_3H_7)(COH)$	456·8	236·0	Present in the essential oil of cumin, and in that of the water hemlock.
Sycocerylic ..	$C_{18}H_{28}O$			

Salicylic aldehyde (salicylol), an oxy-benzoic aldehyde $C_6H_4(OH)COH$, is a fragrant oil, boiling at 385·7° F. (196·5° C.), found in the flowers of the meadow-sweet (*spiræa ulmaria*). By oxidation it forms salicylic acid.

Anisic aldehyde ($C_6H_4(OCH_3)COH$) is a fragrant oily liquid, boiling at 476·6° F. (247° C.), formed by the oxidation of oil of aniseed.

Aldehydes of Series ($C_nH_{2n-9}COH$).

This includes *cinnamic aldehyde*, $CH(C_6H_5)CH.COH$, the essential constituent of oils of cinnamon and cassia. By oxidation it forms cinnamic acid.

Aldehydes of the Dihydric Alcohols.

Of these the only one of any importance is—

Glyoxal, or *oxalic aldehyde* $(COH)_2$, which may be prepared by oxidizing alcohol with nitric acid. It forms, by oxidation, *glyoxalic acid*, COH (COOH).

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CHAPTER XXVII.

THE KETONES.

Constitution—General Preparation—Properties and Reactions.

A ketone is a derivative of an aldehyde, in which the hydrogen atom of the group COH is replaced by an alcohol radical. Thus :—

Acetic aldehyde, CH_3COH, forms $(CH_3)_2CO$, *acetone*.

Propionic aldehyde, C_2H_5COH, forms $(C_2H_5)_2CO$ *diethyl ketone*.

The ketones may also be regarded, either as compounds of carbonic oxide with monad alcoholic radicals, as $(CH_3)_2.CO$, or as compounds of alcohol radicals with acid radicals, as $CH_3.C_2H_3O$ (acetone).

The following are the ketones best known. They correspond to the aldehydes $C_nH_{2n+1}.COH$, or to the fatty acids $C_nH_{2n+1}COOH$.

	NAME.	Formula.	Boiling Point. ° F.	Boiling Point. ° C.
	Dimethyl ketone (acetone)	$CO\{^{CH_3}_{CH_3}$		
	Methyl ethyl ketone	$CO\{^{CH_3}_{C_2H_5}$		
Isomeric	Methyl-isopropyl ketone	$CO\{^{CH_3}_{CH(CH_3)_2}$	199·4	93
Isomeric	Methyl propyl ketone	$CO\{^{CH_3}_{C_3H_7}$	213·8	101
Isomeric	Diethyl ketone (propione)	$CO\{^{C_2H_5}_{C_2H_5}$	212·0	100
Isomeric	Methyl butyl ketone	$CO\{^{CH_3}_{C_4H_9}$	260·6	127
Isomeric	Ethyl propyl ketone	$CO\{^{C_2H_5}_{C_3H_7}$	262·4	128
Isomeric	Methyl-isoamyl ketone	$CO\{^{CH_3}_{C_5H_{11}}$	311·0	155
Isomeric	Dipropyl ketone (butyrone)	$CO\{^{C_3H_7}_{C_3H_7}$	291·2	144

Acetone, the ketone of acetic acid, is the only one of these bodies that has received particular attention. It is a colorless, limpid liquid, having a specific gravity of 0·792, and a vapour density (air=1) of 2·022. It burns with a bright flame, and mixes with water, alcohol, and ether in all proportions.

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We may here note the general preparation and reactions of the ketones of the $CO(C_nH_{2n+1})_2$ group.

Preparation.—1. By the action of carbonic oxide on the sodium organo-metallic compounds, such as sodium ethyle. Thus:—

$$2NaC_2H_5 + CO = Na_2 + CO(C_2H_5)_2.$$
Sodium ethyle + Carbonic oxide = Sodium + Diethyl ketone.

2. By the action of the acid chlorides on the zinc organo-metallic compounds. Thus:—

$$Zn(CH_3)_2 + 2COCH_3Cl = ZnCl_2 + 2[CO(CH_3)_2].$$
Zincic methide + Acetic chloride = Zincic chloride + Acetone.

3. By the oxidation of the secondary monohydric alcohols. Thus:—

$$CH(CH_3)_2(OH) + O = H_2O + CO(CH_3)_2$$
Isopropyl alcohol + Oxygen = Water + Acetone.

4. By the distillation of the baric or calcic salts of the fatty or other monohydric acids, or mixtures thereof. Thus:—

(α.) $$Ca''(C_2H_3O_2)_2 = CaCO_3 + CO(CH_3)_2.$$
Calcic acetate = Calcic carbonate + Acetone.

(β.) $$Ca''(C_5H_9O_2)_2 + Ca''(C_2H_3O_2)_2 = 2CaCO_3 + 2CO\begin{cases} CH_3 \\ C_4H_9. \end{cases}$$
Calcic valerate + Calcic acetate = Calcic carbonate + Methyl-butyl ketone.

General properties and reactions.

Ketones *differ* from aldehydes as follows:—

1. That, whereas aldehydes form acids by spontaneous oxidation, ketones do not.

2. That whereas aldehydes, by reduction with nascent hydrogen, furnish primary alcohols, ketones furnish secondary alcohols.

3. That, whereas aldehydes reduce ammoniacal solutions of argentic oxide, ketones do not.

Ketones *resemble* aldehydes by forming crystalline compounds with hydric-sodic or hydric-potassic sulphite (bisulphites), from which the ketone may be afterwards liberated by an alkali.

With hydrocyanic acid the ketones form cyanides, which, when digested with hydrochloric acid and water, form acids of the lactic series.

With ammonia the ketones, when heated, form basic compounds. Thus acetone forms the base *acetonine*. Thus:—

$$3C_3H_6O + 2NH_3 = C_9H_{18}N_2 + 3H_2O.$$
Acetone + Ammonia = Acetonine + Water.

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CHAPTER XXVIII.

THE ALKALOIDS.

The Natural Alkaloids, Vegetable and Animal—Constitution of the Alkaloids—The Amines (Aniline)—Phosphines—Arsines—Stibines — Bismuthines — Kakodyl — Organo-Boron and Organo-Silicon Compounds—Organo-Metallic Compounds—Amides—Imides—Alkalamides—Nitriles—Tests.

We shall examine the organic bases as follows :—

1. The natural organic alkalies, or alkaloids.
2. The artificial organic bases.

ORGANIC ALKALIES; THE NATURAL ALKALOIDS.

Definition.—A group of organic bodies containing nitrogen, their solutions having an alkaline reaction, and capable of combining with salts to form acids.

History.—In 1803, Derosne discovered narcotine; in 1816, Serturner discovered morphia; since which time numerous alkaloids have been discovered by Pelletier, Robiquet, Caventou, etc.

Natural History.—They are found in all parts of the vegetable, and constitute the active ingredients of plants. They exist in combination with organic acids, which are often as peculiar to the family as the alkaloids, *e.g.*, morphia, etc., with meconic acid; quinine, etc., with kinic acid; strychnia with igasuric acid; atropine with malic acid, etc.

A few alkaloids are found in the animal kingdom, such as urea, kreatine, etc.

Preparation.—The *fixed alkaloids* are extracted from the plant, either by water, or by dilute sulphuric or hydrochloric acid. From this solution the alkaloid is precipitated by an alkali, or by an alkaline earth, such as magnesia. The precipitate is then again dissolved in a dilute acid, decolorized with animal charcoal (which must be used very sparingly, owing to its great power of absorbing the alkaloids and their salts), and reprecipitated from the solution with an alkali. The precipitated alkaloid is then dissolved in boiling alcohol, the solution filtered, and the alkaloid crystallized from the solution.

The *volatile alkaloids* are prepared by distillation from the plant with a very weak alkali. The distillate is always more or less ammoniacal from the decomposition of a portion of the alkaloid. After

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neutralization with oxalic or sulphuric acid, the distillate is evaporated to dryness. The residue is now treated with alcohol, and the upper layer of the mixture drawn off, filtered to separate extraneous matters, and again evaporated. This is treated with a mixture of ether and a potassic hydrate solution, the latter for the purpose of combining with the acid, and the former to dissolve the alkaloid set free. The ethereal layer is then decanted and evaporated.

Properties.—(α.) *Sensible and Physical.* All the alkaloids are solid, except the three which contain no oxygen, viz., nicotine, conia, and sparteine. They all crystallize easily from alcoholic solutions, except quinia, which crystallizes with difficulty, and quinoidine, which is not crystalline. None of them, except the three liquid alkaloids mentioned, have any odor. Their taste is generally more or less bitter. Their physiological action is very energetic. In treating cases of poisoning by them we may say, generally, that the stomach-pump and emetics are indicated, as well as astringent liquids, such as strong tea, etc. Tannic acid precipitates most alkaloids from their aqueous solution.

Action of Heat.—Conia, nicotine, sparteine, theine, and caffeine sublime by heat unchanged: hyoscyamine, cinchonine, and some others partially sublime; piperin, when heated, yields piperdin. All the alkaloids are decomposed (ammoniacal compounds being formed) if the heat applied be sufficient.

Action of Light.—The alkaloids generally have a powerful influence on a polarized beam, some turning it to the right and some to the left.

Quinine solutions are remarkable for their fluorescence.

Action of Electricity.—The salts of the alkaloids (like other salts) liberate the base at the platinode of the battery.

Action of Solvents.—*Water.* The alkaloids generally dissolve in water very slightly, nicotine being one of the most soluble. *Alcohol* dissolves them all, but in varying proportions; thus cinchonine may be separated from quinine by the insolubility of the former in cold alcohol. *Ether* dissolves them all except morphia, cinchonia, sabadilla, strychnia, and brucia. *Chloroform* dissolves strychnia and most of those soluble in ether.

(β.) *Chemical.* The solutions of the alkaloids have generally an alkaline reaction. They act as bases, forming salts with acids. Kreatine is a neutral alkaloid, and not basic.

Action of Acids.—(1.) *Sulphuric acid,* when *concentrated,* slowly decomposes them, strychnia excepted; when *dilute,* it dissolves them and forms salts. With papaverin it strikes a deep blue, thus distinguishing it from all the other opium alkaloids. (2.) *Nitric acid,* sometimes forms nitrates with the alkaloids, and sometimes colored compounds, as in the case of morphia, etc. (3.) *Hydrochloric acid,* forms with many of them additive compounds. With morphia, when heated in sealed tubes, it forms apomorphia. Apocodeine is formed by the action of

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the acid and zinc chloride on codeine. (4.) *Organic acids* combine with many of them, forming generally insoluble salts. For example:—(α.) *tannic acid* precipitates the salts of morphia, narcotine, codeia, cinchonine, quinine, strychnine, brucia, conia, emetine, aconitine, atropine, delphinia, and veratrine. (β.) *Carbazotic acid* precipitates most of the alkaloids.

Action of Alkalies.—Alkalies decompose most of the alkaloids when heated with them with the evolution of ammonia.

Action of Haloids.—(1.) *Chlorine* usually decomposes them, forming hydrochloric acid, which combines with the base itself or with some substitution-compound produced by its action. It forms, (α.) with *strychnia*, a white precipitate; (β.) with *brucia*, *cinchonine*, and *morphia*, yellow precipitates, which change to red, and then to yellow; (γ.) with *narcotine*, a pale red precipitate, which becomes dark red, and then brown; (δ.) with *quinine* (on the addition of ammonia), an emerald-green solution.

(2.) *Bromine* acts in most respects similarly to chlorine.

(3.) *Iodine* combines with most of the alkaloids to produce an insoluble yellow or brown compound of iodine and the alkaloid. This was first noticed by Pelletier in the case of strychnine, and was further investigated by Bouchardat. Herapath has pointed out that the crystalline compound of iodo-sulphate of quinine (Herapathite) $C_{20}H_{24}N_2O_2I_2H_2SO_4(H_2O)_5$ exerts a powerful polarizing action on transmitted light.

Action of metallic salts.

(1.) *Platinic chloride*, forms crystalline compounds with the chlorides of the alkaloids.

(2.) *Mercuric chloride*, forms double salts with the chlorides.

(3.) *Auric chloride*, in some cases, produces a characteristic colored precipitate. Thus, with morphia, it produces a green; with strychnia, a yellow, etc.

(4.) *Ferric chloride*, forms a green compound with morphia.

Action of nascent oxygen.—Nascent oxygen decomposes many of the alkaloids, new compounds being formed. With strychnia, morphia, etc., it gives a characteristic series of tints. (*See* page 10.)

The vegetable alkaloids are extensively used in medicine. As an antiperiodic, quinine is esteemed of great value. The ordinary sulphate of quinine is a basic sulphate, and has the formula $(C_{20}H_{24}N_2O_2)_2,H_2SO_4,8H_2O$. It is very slightly soluble in water. On adding a few drops of sulphuric acid to the basic sulphate suspended in water, a neutral sulphate is formed ($C_{20}H_{24}N_2O_2,H_2SO_4,7H_2O$), which is freely soluble. The tincture of quinine (B.P.) is an alcoholic solution of the basic sulphate. The tinctura quinæ ammoniata (B.P.) is an alcoholic solution of quinia precipitated by ammonia from a solution of a salt. The vinum quinæ is a mixed solution of the neutral sulphate and citrate.

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(A.) Alkaloids of Vegetable Origin.

(1.) The volatile liquid alkaloids which do not contain oxygen :—

NAME.	Formula.	Source.	Properties, etc.
Nicotine	$C_{10}H_{14}N_2$	Tobacco (2–8 per cent.)	A colorless oily liquid, boiling at 464° F. (240° C.). Sp. Gr. 1·027. Soluble in water, etc.
Conine (conia) ..	$C_8H_{15}N$	Hemlock (conium maculatum).	A colorless liquid, boiling at 413·6° F. (212° C.). Sp. Gr. 0·89. An artificial conine has been prepared by distilling *dibutyraldine*, a body formed by digesting normal butyric aldehyde with an alcoholic solution of ammonia. By oxidation conine yields butyric acid.
Sparteine	$C_{10}H_{26}N_2$	Broom (spartium scoparium).	

(2.) The solid alkaloids containing oxygen, arranged according to their Natural Orders :—

NAME.	Formula.	Source.	Properties, etc.
(*a.*) Cinchonaceæ.			
Quinine	$C_{20}H_{24}N_2O_2$	Cinchonas, especially cinchona cordifolia.	Quinine turns the plane of polarization *to the left*; cinchonine *to the right*. Quinine is less disposed to crystallize, and is more soluble in water than cinchonine. Quinine dissolves in cold water (1 in 350), and in alcohol (1 in 2). Cinchonine is insoluble in cold water, and dissolves in boiling alcohol (1 in 35). Cinchonine melts at 221° F. (105° C.).
Cinchonine	$C_{20}H_{24}N_2O$	Cinchonas, especially cinchona condaminea.	
Quinidine	Isomeric c. quinine	Ditto.	Quinidine turns the plane of polarization *to the right*, and cinchonidine *to the left*.
Cinchonidine ..	Isomeric c. cinchonine	Ditto.	
Quinicine	Isomeric c. quinine	Ditto.	Formed by the action of a temperature of 248–266° F. (120–130° C.) for several hours on quinine and cinchonine, or on quinidine and cinchonidine. The action of these bodies on a polarized ray resembles that of quinidine and cinchonidine, but to a very much less marked extent.
Cinchonicine.. ..	Isomeric c. cinchonine	Ditto.	
Quinoidine	Isomeric c. quinine	Ditto.	Called *chinoidine* or amorphous quinine. A brown mass, insoluble in water, soluble in ether, alcohol, and dilute acids. Prepared by the action of heat on quinine.
Aricine (cinchovatine)	$C_{20}H_{26}N_2O_4$	Cusco, or arica bark.	
Emetine	$C_{30}H_{44}N_2O_8$	Ipecacuanha root.	

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NAME.	Formula.	Source.	Properties, etc.
(*b.*) Papaveraceæ.			
Morphia (morphine)	$C_{17}H_{19}NO_3$	From opium, the inspissated juice from the capsule of the papaver somniferum.	Forms prismatic crystals; soluble *in water* (1 in 1000); solution bitter and alkaline; soluble in alcohol (1 in 30); freely soluble in dilute acids and in excess of fixed alkaline hydrates. Melts and burns in air, leaving a small carbon residue.
(Apomorphia) ..	$C_{17}H_{17}NO_2$	Ditto.	Prepared by heating morphia in a sealed tube with hydrochloric acid to 302° F. (150° C.). Very soluble (unlike morphia) in alcohol, ether, and chloroform. It is not a narcotic, but an emetic.
Codeine	$C_{18}H_{21}NO_3$	Ditto.	Prepared from the mother liquor from which the morphia has been crystallised. Forms octahedral crystals. Soluble in water (1 in 80 at 60° F., and 1 in 17 at 212° F.); solution alkaline. Forms salts with acids. It yields apomorphia by prolonged heating with hydrochloric acid.
(Apocodeine)	$C_{18}H_{19}NO_2$	Ditto.	Prepared by heating codeine with hydrochloric acid and chloride of zinc. A mild emetic.
Narcotine	$C_{22}H_{23}NO_7$	Ditto.	Prepared from the insoluble portion (marc) of opium by boiling acetic acid, and precipitation with ammonia. Nearly insoluble in water (1 in 123 at 212° F.). Soluble in acids, but its basic powers are very feeble. With manganese dioxide and H_2SO_4, it forms *opianic acid*. ($C_{10}H_{10}O_5$).
Thebaine (paramorphine)	$C_{19}H_{21}NO_3$	Ditto.	Insoluble in water; soluble in alcohol and ether. It is strongly alkaline and forms crystallizable salts with acids. It is probably the most active of the opium alkaloids.
Papaverine	$C_{20}H_{21}NO_4$	Ditto.	
Pseudo-morphine ..	$C_{17}H_{19}NO_4$	Ditto.	
Narceine	$C_{23}H_{29}NO_9$	Ditto.	
Codamine	$C_{19}H_{23}NO_3$	Ditto.	
Lanthopine	$C_{23}H_{25}NO_4$	Ditto.	
Laudanine	$C_{20}H_{25}NO_3$	Ditto.	
Meconidine	$C_{21}H_{23}NO_4$	Ditto.	
Opianine		Ditto.	
Porphyroxine ..		Ditto.	
(*c.*) Solanaceæ.			
Hyoscyamine (Daturine)	$C_{15}H_{23}NO_3$	Hyoscyamus niger. Datura stramonium.	
Atropine	$C_{17}H_{23}NO_3$	Atropa belladonna.	Sparingly soluble in water. Soluble in alcohol and ether.
Solanine	$C_{43}H_{71}NO_{16}$	Various plants; potato shoots, etc.	

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NAME.	Formula.	Source.	Properties, etc.
(*d.*) **Ranunculaceæ.**			
Delphinine	$C_{24}H_{35}NO_2$	Delphinum staphisagria.	The prepared seeds of stavesacre are used to kill the pediculi of animals.
Aconitine	$C_{30}H_{47}NO_7$	Aconitum napellus.	Soluble in water (1 in 150 at 15° C.; 1 in 50 at 60° C.), in alcohol, and in ether.
(*e.*) **Melanthaceæ.**			
Veratrine (veratria)	$C_{32}H_{52}N_2O_8$	Veratrum sabadilla (white hellebore).	A white powder, insoluble in water; soluble in alcohol, ether, and in acids. Solutions alkaline.
Colchicine		Colchicum autumnale.	
(*f.*) **Strychnaceæ.**			
Strychnine	$C_{21}H_{22}N_2O_2$	Nux vomica, false angustura bark, etc.	Both alkaloids are associated in the plant with igasuric acid. *Strychnine* crystallizes in octahedra; is slightly soluble in water (1 in 7,000); soluble in hot dilute alcohol (1 in 100); insoluble in absolute alcohol, ether, or in alkaline solutions. It forms with acids crystallizable salts.
Brucine	$C_{23}H_{26}N_2O_4$	Ditto.	*Brucia* is readily soluble in alcohol (absolute or dilute) and in boiling water (1 in 500).
(*g.*) **Other orders.**			
Harmaline	$C_{13}H_{14}N_2O$	Peganum harmala. (Russia).	It is soluble in alcohol and in dilute acids. By oxidation it forms *harmine*, $C_{13}H_{12}N_2O$.
Caffeine } Theine }	$C_8H_{10}N_4O_2$	Coffee berries, 1 per cent.; tea leaves, 2–4 per cent.; by the action of methylic iodide on theobromine, at 100° C.	It forms needle crystals; very bitter. When heated it melts and sublimes. Soluble in water (1 in 100 at 60° F.); slightly soluble in alcohol; basic properties feeble. By its oxidation, products are formed closely allied to the uric acid derivatives. With chlorine it yields *amalic acid*, $C_8(CH_3)_4N_4O_7$+aq. With oxidizing agents it yields *cholestrophane* ($C_5H_6N_2O_3$).
Theobromine ..	$C_7H_8N_4O_2$	Theobroma cacao.	White crystals, soluble in a solution of ammonia; not very soluble in pure water.
Berberine	$C_{21}H_{19}NO_5$	Berberis vulgaris (calcumba radix).	A feeble base; crystalline; soluble in water.
Cocaine	$C_{17}H_{21}NO_4$	Coca leaves.	
Piperine	$C_{17}H_{19}NO_3$	Pepper.	Yellow crystals, insoluble in water, soluble in alcohol and acids. By distillation it yields *piperdine* ($C_5H_{11}N$), a colorless liquid boiling at 222·8° F. (106° C.).
Capsicine		Cayenne pepper.	Forms crystallizable salts.
Picocarpine	?	Jaborandi.	
Asparagin	$C_4H_8N_2O_3$	Asparagus (marsh mallow.)	Metameric with malamide.
Physostigmia ..	$C_{30}H_{21}N_3O_4$	Calabar bean.	

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(B.) Alkaloids of Animal Origin.

NAME.	Formula.	Source.	Properties, etc.
Xanthine	$C_5H_4N_4O_2$	Urinary calculi, guanine, urine, all parts of body. Formed by the action of nitrous acid on guanine.	A white amorphous body, soluble in acids, forming salts; slightly soluble in boiling water; soluble in alkaline solutions. Dissolves in HNO_3 without the evolution of any gas, leaving a yellow residue which turns red with ammonia. The hydrochloride is insoluble in water.
Hypoxanthine (Sarcine)	$C_5H_4N_4O$	Flesh of vertebrata, also in blood, liver, etc.	White crystals, soluble in boiling (but not in cold) water, and in dilute acids and alkalies. The hydrochloride is soluble in water.
Guanine	$C_5H_5N_5O$	Guano, excrement of spiders; pancreatic juice.	Colorless crystals; insoluble in water, alcohol, ether, and ammonia; soluble in acids and in a potash solution. Forms salts. By the action of $KClO_3$ and HCl it forms *parabanate* ($C_3H_2N_2O_3$) and *guanadin* (CH_5N_3).
Kreatine	$C_4H_9N_3O_2.2aq$	Flesh, urine, brain.	Colorless crystals; soluble in boiling water; sparingly soluble in cold water (1 in 74); insoluble in alcohol or ether. Solution bitter. Kreatine is a neutral body, combining neither with acids nor alkalies.
Kreatinine	$C_4H_7N_3O$	Ditto.	Prepared by the action of strong acids on kreatine. It forms crystals, soluble in water (1 in 11 at 60° F.), the solution being very alkaline. It forms salts with acids. It evolves *methylia* when heated with soda lime. By boiling with an alkali it forms kreatine.
Sarcosine	$C_3H_7NO_2$	Ditto.	Prepared by boiling kreatine with baryta water.
Urea	CN_2H_4O	Urine.	*Preparation.*—(1.) From urine, by precipitation with oxalic acid. (2.) By heating a solution of ammonic cyanate. (3.) By the decomposition of ammonic carbonate. Forms four-sided crystals, soluble in water and in alcohol; solution neutral. When heated, it first melts and then decomposes. The *pure* solution is permanent in the air, but it decomposes rapidly in urine, owing to the presence of putrefiable organic matter. (*See* Urea.)

Constitution of the Alkaloids.

(1.) *Berzelius* regarded the alkaloids as conjugate bodies of some neutral substance with ammonia (to which latter compound he supposed they owed their alkalinity), founding his theory on the universal

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presence in these bodies of hydrogen and nitrogen. To this, objection was made that it was impossible to detect the presence of ammonia in them.

(2.) *Liebig* regarded them as ammonias, where one atom of hydrogen was replaced by a compound radical; in other words, as compounds of amidogen (NH_2) with a compound radical capable of acting as a hydrogen atom, and not destructive to the original alkalinity. Thus, in *aniline*, $NH_2(C_6H_5)$, H was regarded as being replaced by phenyl (C_6H_5). This view of the composition of aniline was further confirmed by the circumstance that when ammonic phenate was heated, aniline was obtained. Thus—

$$NH_4.C_6H_5O \text{ (\textit{ammonic phenate})} = NH_2(C_6H_5) \text{ \textit{aniline}} + H_2O.$$

Hence an *amide* was regarded as a body derived from an ammoniacal salt by the loss of a water molecule.

(3.) Further investigation has shown that in organic bases—

(α.) One, two or three atoms of the hydrogen of ammonia may be displaced by one, two or three molecules of a univalent compound radical or their equivalent, and that—

(β.) The nitrogen of the ammonia may also be displaced by certain elements, such as phosphorus, arsenic, antimony, etc.

It is important for us to consider here the method of investigation pursued in these enquiries:—

(1.) If ammonia and ethylic iodide (C_2H_5I) be heated in sealed tubes, the apparently conjugate body NH_3,C_2H_5I is formed. When this compound, however, is distilled with potassic hydrate, it yields (not ammonia, but) *potassic iodide* and *ethylamine*, this latter body being ammonia where one of hydrogen has been displaced by one of the alcohol or hydrocarbon radical ethyl (C_2H_5). Thus—

$NH_3.C_2H_5I$	+	KHO	=	$NH_2(C_2H_5)$	+	KI	+	H_2O.
	+	Potassic hydrate	=	Ethyl-amine	+	Potassic iodide	+	Water.

Nevertheless, ethylamine is a colorless alkaline liquid forming salts with acids, boiling at 65·6° F. (18·7° C.), and smelling of ammonia.

(2.) If ethylamine and ethylic iodide be again heated as before in sealed tubes, the compound $NH_2(C_2H_5)C_2H_5I$ will be formed. This, on being distilled with potassic hydrate, furnishes *potassic iodide* and *diethylamine*, this latter being an ammonia where two atoms of hydrogen are replaced by two molecules of the alcohol radical ethyl (C_2H_5). Thus—

$NH_2.C_2H_5.C_2H_5I$	+	KHO	=	$NH(C_2H_5)_2$	+	KI	+	H_2O.
	+	Potassic hydrate	=	Diethylamine	+	Potassic iodide	+	Water.

Nevertheless, diethylamine is a colorless alkaline liquid, boiling at 134·6° F. (57·0° C.), and behaving chemically as ammonia.

(3.) Similarly, *diethylamine*, $NH(C_2H_5)_2$, may be converted into *triethylamine*, $N(C_2H_5)_3$, which is also a colorless alkaline liquid.

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(4.) If triethylamine $N(C_2H_5)_3$ be similarly heated with ethylic iodide, the conjugate compound $N(C_2H_5)_3.C_2H_5I$ is formed.

(5.) Just, however, as we regard the hydriodate of ammonia as an iodide of the hypothetical metal ammonium (NH_4), thus—

$(NH_3)HI$ (*hydriodate of ammonia*)$=(NH_4)I$ (*iodide of ammonium*),

so we may regard the compound $(N(C_2H_5)_3C_2H_5I)$ as the *iodide of tetrethylammonium* $(N(C_2H_5)_4I)$, or, in other words, as a compound where the four atoms of the hydrogen of the metal ammonium have been replaced by four of ethyl.

(6.) On heating this body $(N(C_2H_5)_4I)$ with potassic hydrate, it is not decomposed. When its solution, however, is treated with argentic oxide, an argentic iodide is precipitated, and a solution of tetrethylammonic hydrate is formed. Thus—

$2[N(C_2H_5)_4I]$	+	Ag_2O	+	H_2O	=	$2[N(C_2H_5)_4HO]$	+	$2AgI$.
Iodide of tetrethylammonium	+	Argentic oxide	+	Water	=	Tetrethylammonic hydrate	+	Argentic iodide.

This hydrate, which may be obtained in a crystalline state by evaporation "in vacuo," is an alkaline, caustic, deliquescent body, freely absorbing carbonic anhydride from the air, expelling ammonia from its salts, forming salts with acids, forming soaps with fat, etc. That is, we have a close correspondence, chemically, between this body and potassic and ammonic hydrates. Thus—

KHO;	$(NH_4)HO$;	$(N(C_2H_5)_4)HO$.
Potassic hydrate;	Ammonic hydrate;	Tetrethylammonic hydrate.

(7.) Similarly, the experiments might be conducted on ammonia with the iodides of other alcohol radicals, as methyl (whereby methylamine would be produced); or amyl (forming amylamine, etc.); or one hydrogen may be replaced by one radical, and one by another. Thus, if we act on aniline or phenylamine ($NH_2C_6H_5$), first, with iodide of methyl (CH_3I), and distil with potash, then with iodide of ethyl $(C_2H_5)I$, and distil with potash, and lastly, heat the product with iodide of amyl $(C_5H_{11}I)$, and distil, we obtain a compound formed on the ammonium type, where each hydrogen atom is replaced by a different compound alcohol radical. Thus we obtain—

$$N(C_6H_5)(CH_3)(C_2H_5)(C_5H_{11})HO.$$

Hydrate of phenyl-methyl-ethyl-amyl ammonium.

(8.) From these experiments we learn—

(*a.*) That by heating ammonia with ethylic iodide, and distilling the product with potassic hydrate, we obtain products where the hydrogen is replaced successively by C_2H_5. Thus we obtain—

First; Ethylamine, $NH_2(C_2H_5)$ when H_1 is replaced by C_2H_5.
Secondly; Diethylamine, $NH(C_2H_5)_2$,, H_2 ,, $(C_2H_5)_2$.
Thirdly; Triethylamine, $N(C_2H_5)_3$,, H_3 ,, $(C_2H_5)_3$.

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(β.) That by the further action of ethylic iodide on triethylamine, a compound is formed containing another ethyl molecule, *viz.*, $N(C_2H_5)_4I$, corresponding to the salt NH_4I.

This product, unlike the previous compounds, is not decomposed by the action of potassic hydrate, but may be made to yield a caustic alkaline liquid $N(C_2H_5)_4(HO)$, closely corresponding to $NH_4(HO)$.

9. Adopting a similar method of investigation in examining the constitution of the alkaloids to that above described in the case of ammonia, we ask this question—

How many atoms of hydrogen in the alkaloid can be replaced by an alcohol radical (such as ethyl), by the action upon the alkaloid of iodide of ethyl?

For example:—

Conine has the formula $C_8H_{15}N$. We act upon it with ethylic iodide, and distil the product with potassic hydrate, when we obtain—

$$C_8H_{14}(C_2H_5)N.$$

Thus we learn for certain that one atom of hydrogen can be replaced by C_2H_5.

We again act on the new body formed ($C_8H_{14}(C_2H_5)N$) with ethylic iodide, and we obtain the product $C_8H_{14}(C_2H_5)_2NI$, where, although the body has taken up a new molecule of C_2H_5, nevertheless another hydrogen atom has not been displaced; and further, the new product is not decomposed when treated with potassic hydrate, but is converted by argentic oxide into a soluble base corresponding to $(NH_4)HO$.

Hence our experiments prove that only one hydrogen atom of the compound conine ($C_8H_{15}N$) can be replaced by ethyl, and that therefore the group (C_8H_{14}), supposing conine to be an ammonia, must play the part of two hydrogen atoms. Therefore the formula

$$N\begin{cases}(C_8H_{14})''\\H\end{cases} \text{ or } NH(C_8H_{14})''.$$

represents the constitution of conine as an ammonia.

10. Again, *morphia* has the formula $C_{17}H_{19}NO_3$. Heated with ethylic iodide it forms $C_{17}H_{19}(C_2H_5)NO_3I$, *i.e.*, it refuses to part with any of its hydrogen under the action of ethylic iodide. Hence the formula $N(C_{17}H_{19}O_3)'''$ represents the constitution of morphia, exhibiting it as an ammonia where the group $C_{17}H_{19}O_3$ plays the part of three atoms of hydrogen.

11. Some alkaloids containing two atoms of nitrogen are regarded as being built up on the double ammonia type (N_2H_6); others, containing three of nitrogen, on the treble ammonia type (N_3H_9), etc. Thus:—

$$N_2(C_{20}H_{24}O_2)^{vi}=\text{Quinine};\ N_2(C_{21}H_{22}O_2)^{vi}=\text{Strychnia}.$$

Those bodies that are formed on the type of a single ammonia molecule (NH_3) are termed *monamines;* those on the double ammonia

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type (N_2H_6), as ethylene, $N_2H_4(C_2H_4)''$, *diamines;* those on the treble type (N_3H_9), as diethylene triamine, $N_3H_5(C_2H_4)''_2$, *triamines*, etc.

12. Further, the nitrogen of the ammonias may be replaced by phosphorus, arsenic, antimony, etc. In this way are formed the compounds *triethylarsine*, $As(C_2H_5)_3$ (which, however, is not a true ammonia, inasmuch as it is incapable of forming true salts), and *triethylphosphine*, $P(C_2H_5)_3$, which latter compound is a true ammonia, and forms true salts, such as $P(C_2H_5)_3S$; $P(C_2H_5)_3HO$, etc.

Compound Ammonias.—The Amines.

We have now to consider a class of bases termed the *Amines.*

An amine is an ammonia in which one or more atoms of hydrogen have been replaced by one or more alcohol radicals (that is, a radical which, like CH_3, does not contain oxygen). The amines may be classified as follows:—

(A.) *Monamines: bodies formed on the type of a single ammonia molecule* (NH_3)

These are subdivided into three groups, viz.:—

(α.) *Primary monamines*, where H_1 only is replaced (NH_2R').

(β.) *Secondary monamines*, where H_2 is replaced (NHR'_2).

(γ.) *Tertiary monamines*, where H_3 is replaced (NR'_3).

(B.) *Diamines: bodies formed on the type of a double ammonia molecule* (N_2H_6).

(C.) *Triamines: bodies formed on the type of a treble ammonia molecule* (N_3H_9).

(D.) *Tetramines: bodies formed on the type of a quadruple ammonia molecule* (N_4H_{12}).

(A.) **Monamines.**—*Organic bases formed on the type of a single ammonia molecule* (NH_3). The monamines may be primary, secondary, or tertiary.

(α.) *Primary monamines*, that is, *ammonias* (NH_3), *where one hydrogen atom is replaced by a compound alcohol or hydrocarbon radical. Example:* $NH_2(C_2H_5)$, Ethylamine.

Preparation.—(1.) By the action of the caustic alkalies on cyanates of the alcohol radicals:—

$(C_2H_5)CyO$	+	$2KHO$	=	$NH_2(C_2H_5)$	+	K_2CO_3.
Ethylic cyanate	+	Potassic hydrate	=	Ethyl-amine	+	Potassic carbonate.

2. By the action of the iodides or other haloid compounds of the alcohol radicals on ammonia, and the subsequent decomposition of the compound formed by potassic hydrate:—

(α.)	C_2H_5I	+	NH_3	=	$NH_2(C_2H_5)HI$.	
	Ethylic iodide	+	Ammonia	=	Ethylammonic iodide.	

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(β.) $NH_2(C_2H_5)HI + KHO = NH_2(C_2H_5) + KI + H_2O$.

Ethylammonic iodide + Potassic hydrate = Ethylamine + Potassic iodide + Water.

[This process is also available for the preparation of secondary and tertiary monamines.]

3. By the action of reducing agents on certain nitro derivatives of the hydrocarbons:—

$C_6H_5(NO_2) + 3H_2 = NH_2(C_6H_5) + 2H_2O$.

Nitro-benzene + Hydrogen = Aniline + Water.

(β.) *Secondary monamines*, that is, *ammonias* (NH_3), *where two hydrogen atoms are replaced by two compound radicals, the same or different. Example:* Diethylamine, $NH(C_2H_5)_2$.

Preparation.—By the action of a haloid compound of an alcohol radical on a *primary* monamine (the alcohol radical being the same or different to that contained in the monamine), and the subsequent action on the product of potassic hydrate.

$(C_2H_5)I + NH_2(C_2H_5) = NH(C_2H_5)_2 + HI$.

Ethylic iodide + Ethylamine = Triethylamine + Hydriodic acid.

(γ.) *Tertiary monamines*, that is, *ammonias* (NH_3), *where three hydrogen atoms are replaced by three compound radicals, the same or different. Example:* Triethylamine, $N(C_2H_5)_3$.

Preparation.—By acting in a similar manner to that described above with ethylic iodide on a *secondary* monamine.

$(C_2H_5)I + NH(C_2H_5)_2 = N(C_2H_5)_3 + HI$.

Ethylic iodide + Diethylamine = Triethylamine + Hydriodic acid.

[NOTE.—In practice, when we act on ammonia with ethylic iodide, all these compounds are formed in varying proportions. They cannot be separated by fractional distillation.]

Properties of the Amines.—A tertiary monamine may be known from a primary or a secondary monamine by its forming with ethylic or other like iodide, an iodide which is not decomposed by potassic hydrate. The amines are, with few exceptions, basic compounds. Like ammonia, they are alkaline, and form analogous salts with acids. By the action of alkalies, these salts are decomposed with the separation of the amine, just as with ammonium salts the evolution of ammonia results.

The following is a list of the chief monamines:—

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NAMES.	Formula.	Specific Gravity of Liquid.	Boiling Point. ° F.	Boiling Point. ° C.	Properties.
Ethylamine ..	$NH_2(C_2H_5)$	0·6964 at 88° C.	66·2	19·0	Specific gravity of vapor, 1·57. Ammoniacal odor. Alkaline reaction. Forms salts with acids. Fumes with HCl. Like ammonia, precipitates metallic salts, dissolves AgCl, and produces a blue ppt. with copper salts. Vapor inflammable. Decomposed by HNO_2 into N and ethyl nitrite.
Diethylamine ..	$NH(C_2H_5)_2$		135·5	57·5	A colorless alkaline liquid, soluble in water; forms salts with acids.
Triethylamine ..	$N(C_2H_5)_3$		195·8	91·0	A colorless alkaline liquid. Forms crystalline salts with acids.
Tetrethyl-ammonic hydrate	$N(C_2H_5)_4(OH)$				Crystalline; the crystals decomposed by heat into methylamine, water, and ethylene. The solution is colorless, alkaline and bitter. Closely related to potassic hydrate.
Methylamine ..	$NH_2(CH_3)$	1·08			A gas, alkaline, and of ammoniacal odor. Liquefied at —0·4° F. (—18° C.). One vol. of water at 53·6° (12 ° C.) dissolves 1,040 vols. of gas. Inflammable, and burns with a yellow flame. It occurs in herring brine, and is a product of the action of H on HCN.
Dimethylamine .	$NH(CH_3)_2$				A colorless gas, liquefying at 46·4° F. (8° C.). Smells of NH_3.
Trimethylamine .	$N(CH_3)_3$				A colorless gas, boiling at 48·7° F. (9·3 C.). Smells of ammonia and fish brine.
Tetramethyl-ammonic hydrate	$N(CH_3)_4(OH)$				When heated it yields trimethylamine and methyl alcohol.
Amylamine ..	$NH_2(C_5H_{11})$	0·7503 at 18° C.	199·4	93·0	A colorless liquid, alkaline, having an ammoniacal smell.
Diamylamine ..	$NH(C_5H_{11})_2$		338·0	170·0	An alkaline liquid.
Triamylamine ..	$N(C_5H_{11})_3$		494·6	257·0	A colorless liquid; the salts are sparingly soluble in water.
Tetramyl-ammonic hydrate	$N(C_5H_{11})_4(OH)$				A solid crystalline body; when heated it yields triamylamine, amylene, and water. It is not very soluble in water.
Butylamine ..	$NH_2(C_4H_9)$				
Dibutylamine ..	$NH(C_4H_9)_2$				
Tributylamine ..	$N(C_4H_9)_3$				
Tetrabutyl-ammonic hydrate	$N(C_4H_9)_4(HO)$				

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NAMES.	Formula.	Specific Gravity of Liquid.	Boiling Point. ° F.	Boiling Point. ° C.	Properties.
Allylamine ..	$NH_2(C_3H_5)$				
Diallylamine ..	$NH(C_3H_5)_2$				
Triallylamine ..	$N(C_3H_5)_3$				
Tetra-allyl-ammonic hydrate	$N(C_3H_5)_4(OH)$				
Methyl-ethylamine	$NH(CH_3)(C_2H_5)$				
Methyl-ethyl-phenylamine	$N(CH_3)(C_2H_5)(C_6H_5)$				
Ethyl-amylamine	$NH(C_2H_5)(C_5H_{11})$				
Benzylamine ..	$NH_2(C_7H_7)$		359·6	182·0	A colorless liquid. It absorbs CO_2 and fumes with HCl.
Dibenzylamine..	$NH(C_7H_7)_2$				
Tribenzylamine .	$N(C_7H_7)_3$				
Xylylamine ..	$NH_2(C_8H_9)$		384·8	196·0	Oily liquids, soluble in alcohol and ether, insoluble in water.
Dixylylamine ..	$NH(C_8H_9)_2$				
Trixylylamine ..	$N(C_8H_9)_3$				
Cymylamine ..	$NH_2(C_{10}H_{13})$		536·0	280·0	Oily liquids.
Dicymylamine ..	$NH(C_{10}H_{13})_2$		572·0	300·0	
Tricymylamine..	$N(C_{10}H_{13})_3$				A crystalline solid. Melts at 177·8° F. (81° C.).
Naphthalidine ..	$NH_2(C_{10}H_7)$				A crystalline solid. Prepared by the action of NH_4HS on an alcoholic solution of nitronaphthalene. Forms salts.
Aniline (phenylamine)	$NH_2(C_6H_5)$	1·028	359·6	182·0	*See* page 663.
Toluidine.. .. (tolylamine ; amidotoluene)	$NH_2(C_6H_4Me)$ or $NH_2(C_7H_7)$				Exists in three forms; as *para-toluidine*, a crystalline solid, melting at 45° C. : *ortho-toluidine*, a liquid, Sp. Gr. 0·998, boiling at 197° C., becoming rose colored on exposure to air; and *meta-toluidine*, a crystalline solid melting at 57° C.
Conine	$NH(C_8H_{14})''$				
Piperidine	$NH(C_5H_{10})''$				
Pyrrol	$N(C_4H_5)$	1·077	271·4	133·0	Prepared from animal oils. A colorless liquid, turns a piece of fir wood moistened with HCl purple.
Pyridine	$N(C_5H_5)'''$		242·6	117·0	Prepared from coal tar naphtha, and by heating amyl nitrate with phosphoric anhydride $C_5H_{11}NO_3 - 3H_2O = N(C_5H_5)$
Picoline (paraniline)	$N(C_6H_7)'''$	0·955	271·4	133·0	A liquid prepared from coal tar naphtha.
Lutidine	$N(C_7H_9)'''$		309·2	154·0	Do.
Collidine (xylidine)	$N(C_8H_{11})'''$		419·0	215·0	Do.

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NAMES.	Formula.	Specific Gravity of liquid.	Boiling Point. ° F.	Boiling Point. ° C.	Properties.
Chinoline	$N(C_9H_7)$	1·081	455·0	235·0	By distilling quinine, etc., with a strong solution of potassic hydrate. A colorless oily liquid forming salts with acids.
Parvoline (cumidine)	$N(C_9H_{13})'''$		370·4	188·0	A liquid prepared from coal tar naphtha.
Cymidine (coridine)	$N(C_{10}H_{15})'''$		482·0	250·0	
Rubidine	$N(C_{11}H_{17})'''$		446·0	230·0	
Viridine	$N(C_{12}H_{19})'''$		483·8	251·0	

(B.) **Diamines.**—*Organic bases formed on the type of a double ammonia molecule* (N_2H_6).

Preparation.—By the action of a haloid salt of a diatomic alcohol radical (as ethene (ethylene), C_2H_4, etc.), on ammonia. Thus:—

$$2NH_3 + (C_2H_4)''Br_2 = N_2H_4(C_2H_4)'' + 2HBr.$$

Ammonia + Ethylene dibromide = Ethylene diamine + Hydrobromic acid.

That is, $N_2H_4(C_2H_4)''$ represents a double ammonia molecule (N_2H_6), where two atoms of hydrogen have been replaced by the diatomic radical $(C_2H_4)''$.

Just as $2(NH_4,HO)$ represents a double molecule of a hydrate of ammonium (NH_4), so $(N_2H_4(C_2H_4)''_2,H_2O_2)$ represents a molecule of the fixed alkaline base, *hydrate of ethylene diammonium.*

The following table represents some of the diamines:—

Name.	Formula.	Boiling point. ° F.	Boiling point. ° C.	Properties.
Ethylene diamine ..	$N_2H_4(C_2H_4)''$	242·6	117·0	An oily liquid.
Urea	$N_2H_4(CO)''$			
Sulphur-urea	$N_2H_4(CS)''$			
Ethyl-urea	$N_2H_3(C_2H_5)'(CO)''$			
Sulpho-phenyl-urea..	$N_2H_3(C_6H_5)'(CS)''$			

(C.) **Triamines.**—*Organic bases formed on the type of a treble ammonia molecule* (N_3H_9).

To this class belong many of the bases of the aniline colors, such as *rosaniline*, etc.

There are certain other amines to which mere reference must suffice, it being impossible to classify them.

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NAME.	Formula.	Sp. Gr.	Properties.
Furfurine	$C_{15}H_{12}N_2O_3$		Prepared by boiling *furfuramide*, a body formed by the action of ammonia on a solution of furfurol ($C_5H_4O_2$) in potassic hydrate. A powerful base soluble in boiling water (1 in 135), in alcohol and in ether. Solutions alkaline; salts bitter.
Benzoline; (amarine)	$C_{21}H_{18}N_2$		By the action of potassic hydrate on hydrobenzamide (C_7H_6O). A solid substance insoluble in water.
Thialdine	$C_6H_{13}NS_2$	1·191	Forms solid, highly refracting crystals. It is volatile, and yields salts with acids.

Aniline ($C_6H_7N=93$).

Specific Gravity, 1·028; *Freezing point*, 17·6° F. (−8° C.); *Boiling point*, 359·6° F. (182° C.); *Molecular volume*, $\boxed{\ |\ |\ }$.

Origin of Name.—From the indigo plant, *Indigofera anil.*

Synonyms.—*Phenylamine* (regarding it as an ammonia derivative); *Phenylia*; *Amido-benzene.*

Constitution.—Aniline may be regarded either (1) as an ammonia derivative, where H_1 is displaced by one of phenyl (C_6H_5) :—hence called *phenylamine*, $NH_2(C_6H_5)'$; or (2) as a derivative of benzoic acid, hence called *amido-benzene*, $C_6H_5(NH_2)$.

For the following reasons we are led to regard aniline as an ammonia:—

(α.) *Its behaviour with ethylic iodide.*—Thus it forms successively ethyl-phenyl-, diethyl-phenyl-, and triethyl-phenyl-ammonic iodide, the two former yielding

Ethyl-phenyl amine $\left.\begin{matrix}C_6H_7\\C_2H_5\\H\end{matrix}\right\}N$; and *Diethyl-phenyl amine* $\left.\begin{matrix}C_6H_7\\C_2H_5\\C_2H_5\end{matrix}\right\}N$

respectively, when treated with potassic hydrate; the last yielding triethyl-phenylammonic hydrate when treated with water and argentic oxide.

This reaction corresponds to ammonia, as already explained (page 655).

(β.) As potassic hydrate separates NH_3 from ammonic salts, so it separates aniline (NC_6H_7) from aniline salts.

(γ.) By heating together phenic acid and ammonia in an hermetically sealed tube, aniline is formed by the substitution of phenyl (C_6H_5) for hydrogen.

(δ.) The salts of aniline correspond to the salts of ammonia.

Preparation.—(1.) By distilling powdered indigo with a saturated solution of potassic hydrate:—

C_8H_5NO	+	$4KHO$	+	H_2O	=	$2H_2$	+	$2K_2CO_3$	+	C_6H_7N.
Indigo	+	Potash	+	Water	=	Hydrogen	+	Potassic carbonate	+	Aniline.

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(2.) By heating together ammonia and phenol for two or three weeks in sealed tubes. (Laurent.)

$$C_6H_5(OH) + NH_3 = H_2O + C_6H_5(NH_2)\ [\text{or } C_6H_7N].$$
Phenol + Ammonia = Water + Aniline.

(3.) By the action of reducing agents on nitro-benzene; such as,—

(α.) *Sulphuretted hydrogen* (Zinin)—

$$C_6H_5(NO_2) + 3H_2S = 2H_2O + S_3 + C_6H_7N.$$
Nitro-benzene + Sulphuretted hydrogen = Water + Sulphur + Aniline.

(β.) *Ferrous acetate* (Béchamp).

(γ.) *Dilute sulphuric acid and zinc* (*i.e. nascent hydrogen*).

$$C_6H_5(NO_2) + 3H_2 = 2H_2O + C_6H_7N.$$
Nitro-benzene + Hydrogen = Water + Aniline.

[In the commercial manufacture of aniline, nitro-benzene is heated in a retort with glacial acetic acid and iron filings, when the aniline distils over, together with water, in which the aniline sinks. It is then separated, any acetate present being decomposed with an alkali, and redistilled. All the aniline of commerce contains toluidine, commercial benzene always containing toluene.]

Aniline is found amongst the products of the distillation of coal and other organic matters.

Properties.—(α.) *Sensible.* Aniline when pure has a slightly brown tint, and is a thin oily liquid, having a faint odor and a burning taste. It is an active poison.

(β.) *Physical.*—Specific gravity, 1·028. It is very volatile. It freezes at 17·6° F. (—8° C.), forming a crystalline mass. It boils at 359·6° F. (182° C.). It is slightly soluble in water (forming, possibly, a hydrate), and is very soluble in alcohol and ether.

(γ.) *Chemical.*—It is not alkaline to test-paper, but its vapor forms white fumes with hydrochloric acid. By contact with air it becomes of a dark color and of resinous consistency. By the action upon it of oxidizing agents the various aniline colors are formed. With the haloids (but not by their direct union) it forms substitution products, as chlor- or brom-aniline (C_6H_6ClN), dichlor- or dibrom-aniline ($C_6H_5Cl_2N$), and trichlor- or tribrom-aniline ($C_6H_6Cl_3N$). The first two of these haloid substitution compounds are bases, and form salts; but the last compound, *i.e.* where the substitution is complete, is neutral. Aniline is a powerful organic base, and with acids forms crystalline salts.

Numerous other substitution products of aniline have been prepared, as, *e.g.*, *nitraniline*, $C_6H_6(NO_2)N$, a body existing in two modifications; *dinitraniline*, $C_6H_5(NO_2)_2N$; *diphenylamine*, $NH(C_6H_5)_2$, etc. With cyanogen it forms the compound *cyan-aniline* $(C_6H_7N)_2Cy_2$.

When nitrous acid is passed (α.) into aniline, *phenol*, nitrogen, and

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water are evolved; but when the acid is passed through (β.) an alcoholic solution of aniline, *azodiphenyl-diamine* and water are formed. (γ.) If azodiphenyl-diamine be treated with nitrous acid, an explosive body, *diazo-diphenyldiamine*, is produced.

These several reactions may be shown as follows:

(α.) $C_6H_7N + HNO_2 = C_6H_6O + H_2O + N_2$.
Aniline + Nitrous acid = Phenol + Water + Nitrogen.

(β.) $2C_6H_7N + HNO_2 = C_{12}H_{11}N_3 + 2H_2O$.
Aniline + Nitrous acid = Azodiphenyl-diamine + Water.

(γ.) $C_{12}H_{11}N_3 + NO_3 = C_{12}H_8N_4 + 2H_2O$.
Azodiphenyl-diamine + Nitrous acid = Diazo-diphenyl-diamine + Water.

With an *alkaline hypochlorite* aniline forms a violet (mauve). With *chromic acid* it gives a bluish-black precipitate.

Uses.—For the manufacture of dyes.

Homologous with aniline is the base,

Toluidine (C_7H_9N). It is found in three states—(1) as a *solid* (*paratoluidine*), melting at 113° F. (45° C.), and boiling at 401° F. (205° C.); (2), as *a liquid* (*orthotoluidine*), boiling at 386·6° F. (197° C.); specific gravity, 0·998°; and (3), as a *second solid* (*metatoluidine*), melting at 134·6° F. (57° C.), and boiling at 464° F. (240° C.).

Coal-Tar Dyes: Aniline Colors.

Aniline Purple; Mauve.—*Preparation.*—By the action of sulphuric acid and potassic bichromate on aniline. The mauve is extracted from the residue by hot alcohol.

Properties.—It is insoluble (or nearly so), in water, ether, etc., but is freely soluble in alcohol, acetic acid, etc. The base of this compound is a colorless body, called mauveïne ($C_{27}H_{24}N_4$).

Aniline Red; Rosaniline.—*Preparation.*—By the action on aniline of various reagents, such as stannic chloride, mercuric salts, arsenic acid, and many other oxidizing agents. The base, *rosaniline*, is colorless, and has the composition $C_{20}H_{19}N_3$. It is freely soluble in alcohol, but is scarcely at all soluble in water. From rosaniline, by the replacement of hydrogen by alcohol radicals, various other bases forming coloring matters with acids, have been formed. By the action upon it of ammonic sulphide, or of free hydrogen, *leucaniline* $C_{20}H_{21}N_3$ is formed, the hydrochlorate of which is white, but is converted by oxidizing agents into rosaniline.

To obtain a red from aniline, it is said to be essential that the aniline should contain toluidine, inasmuch as pure aniline (*i. e.*, aniline derived from benzoic acid) yields no red coloring bodies.

Aniline Blue; Triphenyl-rosaniline. ($C_{20}H_{16}(C_6H_5)_3N_3$).—*Pre-*

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paration.—By boiling rosaniline with an excess of aniline at from 300° to 320° F. (150°-160° C.).

Aniline Green. (α.)—*Aldehyde green.*—*Preparation.*—By adding aldehyde to a solution of magenta and sulphuric acid, and treating the product with sodic thiosulphate.

(β.) *Iodine Green.*—By the action of methyl- or ethyl- iodide on aniline violets.

Aniline Yellow contains a well-defined base called *chrysaniline* ($C_{20}H_{17}N_3$). It is found amongst the secondary products of aniline red. Its nitrate is insoluble in water.

Phosphines : Arsines : Stibines : Bismuthines.

Phosphorus, arsenic and antimony, like nitrogen, form compounds with three atoms of hydrogen, viz., PH_3, AsH_3, SbH_3, which bodies also form compounds analogous to the amines (termed *phosphines, arsines,* &c.), excepting that in AsH_3 and in SbH_3, the replacement of the hydrogen is always complete.

Properties.—They are mostly liquids, having a very strong odor. Many of them are spontaneously inflammable. They have great affinity for oxygen and for the haloids, forming compounds in which the metal is quin-quivalent. Thus we have *stibethyl oxide*, $Sb^v(C_2H_5)_3O$; *stibethyl chloride*, $Sb^v(C_2H_5)_3Cl_2$, etc. The tertiary compounds form, with ethylic or methylic iodide, compounds from which argentic oxide separates the hydrates; thus—

$P(CH_3)_4HO$;	$P(C_2H_5)_4(HO)$;	$As(C_2H_5)_4(HO)$;	$Sb(C_5H_{11})_4(HO)$, etc.
Hydrate of tetramethyl phosphine;	Hydrate of tetrethyl phosphine;	Hydrate of tetrethyl arsine;	Hydrate of tetramyl stibine.

Some of these compounds are stated in the following table:—

Name.	Formula.	Sp. Gr.	Boiling point.		Properties.
			F.	C.	
Phosphines.					
Methyl phosphine ..	$PH_2(CH_3)$		6·8	−14·0	
Dimethyl phosphine ..	$PH(CH_3)_2$		77·0	25·0	
Trimethyl phosphine ..	$P(CH_3)_3$		105·8	41·0	A colorless oil, very volatile.
Ethyl phosphine	$PH_2(C_2H_5)$		77·0	25·0	
Diethyl phosphine ..	$PH(C_2H_5)_2$		185·0	85·0	
Triethyl phosphine ..	$P(C_2H_5)_3$		261·5	127·5	Prepared by the action of phosphorous chloride (PCl_3) on zinc ethyl. A colorless oil, oxidizes in air, and explodes by heat.
Arsines.					
Trimethyl arsine ..	$As(CH_3)_3$		248·0	120·0	Prepared by the action of methylic iodide on an alloy of arsenic and sodium.

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Name.	Formula.	Sp. Gr.	Boiling point.		Properties.
			° F.	° C.	
Arsines (cont.).					
Triethyl arsine	$As(C_2H_5)_3$		284·0	140·0	Prepared by the action of ethylic iodide on an alloy of arsenic and sodium. A colorless liquid, having a very disagreeable odor.
Stibines.					
Trimethyl stibine ..	$Sb(CH_3)_3$				
Triethyl stibine .. .. (Stibethyl)	$Sb(C_2H_5)_3$		316·4	158·0	Prepared by the action of ethylic iodide on an alloy of antimony and potassium. Odor of onions; combines powerfully with oxygen and the haloids.
Triamyl stibine	$Sb(C_5H_{11})_3$				
Bismuthine.					
Triethyl bismuthine ..	$Bi(C_2H_5)_3$	1·82			Prepared by the action of ethylic iodide on an alloy of bismuth and potassium. A yellow nauseous liquid.

Arsen-mono-methyl.—Kakodyl.

It will be convenient to examine these bodies here, which, however, it must be specially noted, are not formed on the ammonia type.

Arsen-mono-methyl; $As(CH_3)$. This radical is not known in the free state. It forms compounds by combining with either two or four atoms of a univalent element or compound radical, or their equivalent. Thus it forms a *dichloride* $As'''(CH_3)Cl_2$, which is a heavy, very poisonous liquid, and a *tetrachloride*, $As^v(CH_3)Cl_4$, a stable crystalline solid; *an oxide*, $As'''(CH_3)O$, a bibasic acid, *arsen-methyllic acid*, $As^v(CH_3)O''(OH)_2$, *a sulphide*, $As'''(CH_3)S$, etc.

Kakodyl (Cacodyl); *Arsen-dimethyl* ($As'''_2(CH_3)_4$), or $As(CH_3)_2$ Boils at 338° F. (170° C.). Freezes at 42·8° F. (6° C.).

Preparation.—(α.) By distilling together potassic acetate and arsenious oxide, a spontaneously inflammable liquid is formed, called *alkarsin* (*Cadet's fuming liquid*).

$$4KC_2H_3O_2 + As_2O_3 = As_2(CH_3)_4O + 2K_2CO_3 + 2CO_2$$

Potassic acetate + Arsenious oxide = Alkarsin + Potassic carbonate + Carbonic anhydride.

(β.) This alkarsin combines with acids to form salts. Thus, by acting upon it with hydrochloric acid it forms a chloride, thus—

$$As_2(CH_3)_4O + 2HCl = As_2(CH_3)_4Cl_2 + H_2O.$$

Alkarsin + Hydrochloric acid = Chloride of alkarsin + Water.

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(γ.) By distilling this chloride of alkarsin with zinc, kakodyl [$As_2(CH_3)_4$] is obtained, together with zincic chloride, which latter product may be dissolved out with water.

Properties.—(α.) *Physical.* Kakodyl is a colorless, transparent, oily liquid, having a most offensive odor (κάκος bad). It is intensely poisonous. It boils at 338° F. (170° C.). At a heat below redness it resolves itself into arsenicum, methane, and ethene:—

$As_2(CH_3)_4$	=	As_2	+	C_2H_4	+	$2CH_4$.
Kakodyl	=	Arsenicum	+	Ethene (1 vol.)	+	Methane (2 vols.)

(β.) *Chemical.* Kakodyl catches fire spontaneously when poured into oxygen, air, or chlorine, and it also combines directly with sulphur. If the air in contact with it be limited, it forms kakodyl oxide, $As_2(CH_3)_4O$, and in the presence of water, *kakodylic acid*. The following are some of its compounds:—

Name.	Formula.	Preparation, Properties, etc.
Kakodyl oxide ..	$As_2'''(CH_3)_4O''$	*Preparation.* — By the slow oxidation of kakodyl. *Properties.*—A colorless, pungent, oily liquid. Boils at 120° C. It explodes when heated to 190·4° F. (88° C.), but does not fire in the air. It is insoluble in water, but is soluble in HCl, HBr and HI.
Kakodyl dioxide ..	$As_2(CH_3)_4O_2$	Decomposed by water into kakodyl oxide and kakodylic acid, $2(As_2CH_4O_2)+H_2O=As_2(CH_3)_4O+2As(CH_3)_2O(HO)$.
Kakodylic acid (alkargen)	$As^v(CH_3)_2O''(HO)$	*Preparation.*—By the slow oxidation of kakodyl in the presence of moisture. *Properties.*—Deliquescent crystals, soluble in water and in alcohol: reaction acid. It is very stable, and is not even affected by boiling nitro-hydrochloric acid. It is decomposed by dry HI. It combines with HCl. It is decomposed by PCl_5, forming a trichloride. It is not poisonous.
Kakodyl chloride .. (Arsen chloro-dimethide)	$As'''(CH_3)_2Cl$	*Preparation.*—By distilling alkarsin with HCl. *Properties.*—A colorless liquid, volatile at ordinary temperatures. Soluble in alcohol; insoluble in water or in ether. The vapor inflammable, and has a specific gravity of 4·56°.
Kakodyl trichloride	$As^v(CH_3)_2Cl_3$	*Preparation.*—By the action of PCl_5 on Kakodylic acid.
Kakodyl iodide ..	$As(CH_3)_2I$	*Preparation.*—By distilling alkarsin with a strong solution of HI.
Kakodyl cyanide ..	$As(CH_3)_2Cy$	*Preparation.* — By distilling alkarsin with HCy, or by the action of oxide of kakodyl on cyanide of mercury. *Properties.*—Crystalline. Melts at 91·4° F. (33° C.), and boils at 284° F. (140° C.). The vapor is very poisonous.
Kakodyl sulphide ..	$As_2(CH_3)_4S$	A liquid, boiling at about 248° F. (120° C.).
Kakodyl disulphide	$As_2(CH_3)_4S_2$	*Preparation.*—By the action of H_2S on kakodylic acid. *Properties.*—It yields salts of sulpho-kakodylic acid. $As^v(CH_3)_2S_2H$.

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Organo-Boron, -Silicon, and -Metallic Compounds.

Boron, silicon, and certain metals, also combine with alcohol radicals, forming compounds built up on the ammonia type.

Organo-Boron Compounds.

These are compounds of boron with hydrocarbon radicals (as methyl; CH_3), the boron being directly combined with the carbon—

Name.	Formula.	Preparations, Properties, etc.
Boric methide ..	$B(CH_3)_3$	*Preparation.*—By adding an ethereal solution of zinc methide to boracic ether $2[B(C_2H_5)_3O_3] + 3[Zn(CH_3)_2] = 2[B(CH_3)_3] + 3[Zn(C_2H_5)_2O_2]$. *Properties.*—A heavy pungent gas; specific gravity 1·93; condenses at 50° F. (10° C.), under a pressure of four atmospheres; inflames spontaneously in air; combines with ammonia to form ammonia boric methide $(NH_3, B(CH_3)_3)$.
Boric ethide (Triborethyl) ..	$B(C_2H_5)_3$	*Preparation.*—By adding an ethereal solution of zinc ethide to boracic ether. *Properties.*—A colorless liquid; specific gravity, 0·696; boils at 203° F. (95° C.); inflames spontaneously in air, burning with a green flame. It combines with ammonia to form ammonia boric ethide, NH_3, $B(C_2H_5)_3$.

Organo-Silicon Compounds.

Compounds of silicon with hydrocarbon radicals, the silicon being directly combined with the carbon—

		Boiling Pt.		
		° F.	° C.	
Silicic methide ..	$Si(CH_3)_4$	86·9	30·5	*Preparation.*—By the action of zinc methide on silicic chloride.
Silicic ethide ..	$Si(C_2H_5)_4$	306·5	152·5	*Preparation.*—By the action of zinc ethide on silicic chloride.
Derivatives.				
Silicic methylate ..	$Si(CH_3)_4O_4$	249·8	121·0	
Silicic ethylate ..	$Si(C_2H_5)_4O_4$	331·7	166·5	

Organo-Metallic Bodies.

These are compounds of a metal and an alcohol radical, the metal being directly combined with the carbon of the radical. Thus zinc

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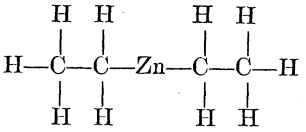
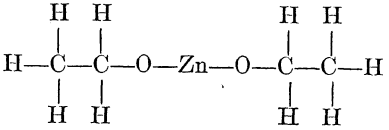
ethyl, $Zn(C_2H_5)_2$ is an organo-metallic body, and may be represented thus—



whilst zinc ethylate $Zn(C_2H_5)_2O_2$ is not an organo-metallic body (for the metal is not directly connected with the carbon of the radical), but is simply an organic body containing zinc, and may be represented thus—



Preparation.—(1.) By the action of a metal on an iodide of the monad positive radical under the influence of heat, or sometimes of light—

$2(C_2H_5)I$	+	Zn_2	=	$Zn(C_2H_5)_2$	+	ZnI_2.
Ethylic iodide	+	Zinc	=	Zincic ethyle	+	Zincic iodide.

(2.) By the action of alloys of the metals with K or Na, on an iodide of the monad positive radicals—

$2(C_2H_5)I$	+	$HgNa_2$	=	$Hg''(C_2H_5)_2$	+	2NaI.
Ethylic iodide	+	Sodium and mercury alloy	=	Mercuric ethide	+	Sodic iodide.

(3.) By the action of haloid salts of the metals (as $Sn^{iv}Cl_4$), on the zinc organo-metallic compounds—

$SnCl_4$	+	$2[Zn(C_2H_5)_2]$	=	$Sn(C_2H_5)_4$	+	2ZnCl.
Stannic chloride	+	Zinc ethyle	=	Stannic ethyle	+	Zincic chloride.

(4.) By the displacement of one metal in an organo-metallic compound, by a second and more positive metal—

$Hg(C_5H_{11})_2$	+	Zn	=	$Zn(C_5H_{11})_2$	+	Hg.
Mercuric amylide	+	Zinc	=	Zincic amylide	+	Mercury.

Some of these organo-metallic compounds are represented in the following table:—

Name.	Formula.	
Sodic ethide	$Na(C_2H_5)$	Corresponding to NaCl
Zincic ethide..	$Zn(C_2H_5)_2$	,, $ZnCl_2$
,, methide	$Zn(CH_3)_2$	,, $ZnCl_2$
,, amylide	$Zn(C_5H_{11})_2$	,, $ZnCl_2$
Mercuric methide.. ..	$Hg(CH_3)_2$	,, $HgCl_2$
,, ethide	$Hg(C_2H_5)_2$	,, $HgCl_2$
Stannous ethide	$Sn(C_2H_5)_2$	,, $Sn''Cl_2$
Stannic ethide	$Sn(C_2H_5)_4$	,, $Sn^{iv}Cl_4$
Plumbic ethide	$Pb(C_2H_5)_4$	,, PbO_2
Aluminic methide.. ..	$Al_2(CH_3)_6$	,, Al_2Cl_6

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For further details as to the properties of these organo-metallic bodies, *see* Frankland's Lecture Notes, Vol. ii., p. 227.

Amides; Imides; Alkalamides; Nitriles.

An amide is a compound of amidogen (NH_2) and an acid radical. We may regard the amides either as:—

(1.) Derivatives of ammonia; or as

(2.) Derivatives of organic acids.

1. *As derivatives of ammonia;* that is, an *amide* may be regarded as an ammonia where one or more atoms of hydrogen are replaced by *an acid radical, i.e.*, a radical containing oxygen (such as C_2H_3O, the radical of acetic acid).

[N.B.—An *amine* is regarded as an ammonia where one or more atoms of hydrogen are replaced by *an alcohol or hydrocarbon radical, i.e.*, a radical containing no oxygen (as CH_3, methyle, etc.)].

Thus the amides may be obtained from their ammonic salts by the abstraction of water, and may be converted into their ammonic salts by the assimilation of water.

Thus by driving off water by heat from ammonic acetate or ammonic oxalate we obtain acetamide and oxamide respectively. Thus:—

$$\underset{\text{Ammonic acetate}}{NH_4(C_2H_3O_2)} - \underset{\text{Water}}{H_2O} = \underset{\text{Acetamide}}{NH_2(C_2H_3O)}\,; \quad \underset{\text{Ammonic oxalate}}{(NH_4)_2(C_2O_4)} - \underset{\text{Water}}{(H_2O)_2} = \underset{\text{Oxamide.}}{(NH_2)_2C_2O_2}.$$

and conversely, by heating acetamide and oxamide with water, we reproduce from them ammonic acetate and ammonic oxalate.

2. *As derivatives of acids:* that is, an amide may be regarded as an acid where the group (HO) is replaced by amidogen (NH_2).

Thus, by acting with ammonia on a chlor-acid, as acetylic chloride (which is acetic acid, $C_2H_3O(HO)$, where Cl has replaced the group (HO)), we obtain acetamide. Thus:—

$$\underset{\text{Acetylic chloride}}{C_2H_3O.Cl} + \underset{\text{Ammonia}}{NH_3} = \underset{\text{Acetamide}}{C_2H_3O(NH_2)} + \underset{\text{Hydrochloric acid.}}{HCl}.$$

Thus it would appear that we may formulate the amides in two ways. For example: acetamide and oxamide.

(1.) As *ammonia derivatives* they may be stated as follows:—

$$N\begin{cases} H \\ H \\ (C_2H_3O) \end{cases} = \underset{\text{Acetamide;}}{NH_2(C_2H_3O)}\,; \quad N_2\begin{cases} H_2 \\ H_2 \\ (C_2O_2)'' \end{cases} = \underset{\text{Oxamide.}}{(NH_2)_2(C_2O_2)}.$$

(2.) As *acid derivatives* (of acetic acid, $CH_3CO(HO)$, and of oxalic acid, $C_2O_2(HO)_2$ respectively), as follows:—

$$\underset{\text{Acetamide}}{C_2H_3O(NH_2)}, \quad \text{or} \quad \underset{\text{Oxamide.}}{C_2O_2(NH_2)_2}.$$

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An imide is an ammonia derivative where two of the three hydrogen atoms are replaced by one molecule of a bivalent acid radical.

An imide, therefore, is a compound of imidogen $(NH)''$, *and a bivalent acid radical.* Thus:—

$$(NH)''(C_4H_4O_2)''=\text{Succinimide.}$$

An alkalamide may be regarded as an ammonia derivative where the hydrogen is partly replaced by an alcohol (positive) radical, and partly by an acid radical: *e.g.*—

$$\text{Ethyl acetamide}=NH\,(C_2H_5)\,(C_2H_3O).$$

There are no primary alkalamides, inasmuch as two atoms of hydrogen in every case must be substituted.

We append tables of the chief amides of monatomic, diatomic, and triatomic acids.

I.—Amides of Monatomic Acids.

	Name.	Formula.	Acid from which derived	Properties.
Primary monamides..	Acetamide	$NH_2(C_2H_3O)$	Acetic acid $C_2H_3O(OH)$	A white solid; melts at 172·4° F. (78° C.), and boils at 429·8° F. (221° C.)
	Benzamide	$NH_2(C_7H_5O)$	Benzoic acid $C_7H_5O(OH)$	A crystalline body; melts at 239° F. (115° C.), and volatilizes unchanged at 546·8° F. (286° C.)
Secondary monamides	Diacetamide Succinimide	$NH(C_2H_3O)_2$ $NH(C_4H_4O_2)''$		These containing trivalent acid radicals, are called imides.
Secondary monamides or secondary *alkalamides*	Ethyl acetamide	$NH(C_2H_5)(C_2H_3O)$		
Tertiary monamides, or tertiary alkalamides	Ethyl diacetamide	$N(C_2H_5)(C_2H_3O)_2$		

II.—Amides of Diatomic Acids.

These are of three kinds—

(*a.*) *An acid amide* or *amic acid*, prepared from an acid ammonic salt by the abstraction of one water molecule, *e.g.*:—

$(NH_4)C_4H_5O_4$ (acid ammonic succinate)—H_2O=$(C_4H_4O_2)''(NH_2)(OH)$(succinamic acid)

(*β.*) A *neutral monamide* or *imide*, prepared from an acid ammonic salt by the abstraction of two water molecules; *e.g.*:—

$(NH_4)C_4H_5O_4$ (acid ammonic succinate) — $(H_2O)_2$=$(C_4H_4O_2)''(NH)''$ (succinimide)

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(γ.) A *neutral diamide* prepared from a neutral ammonic salt, by the abstraction of two water molecules; *e.g.* :—

$(NH_4)_2C_4H_4O_4$ (neutral ammonic succinate) $= (C_4H_4O_2)''(NH_2)_2$ (succinamide) $+ 2H_2O$.

Name.		Formula.	Properties.
Ammonia salts of oxalic acid $C_2O_2(HO)_2$	Oxamic acid ..	$(C_2O_2)''(NH_2)(OH)$	White crystals; forms salts. If NH_2 be replaced by ethyl, an acid oxamic ether is formed, but if the (OH) be replaced by ethyl, a neutral ether results.
	Oximide (?) ..	(?)	
	Oxamide	$(C_2O_2)''(NH_2)_2$	Formed also by the action of HCN on H_2O_2. Decomposed by heat into HCN and urea $C_2O_2(NH_2)_2 = CO+CO_2+NH_3+CyH+CN_2H_4O$
Ammonia salts of succinic acid $C_4H_4O_2(OH)_2$	Succinamic acid	$(C_4H_4O_2)''(NH_2)(OH)$	
	Succinimide ..	$(C_4H_4O_2)''(NH)''$	
	Succinamide ..	$(C_4H_4O_2)''(NH_2)_2$	
Ammonia salts of carbonic acid $CO(OH)_2$	Carbamic acid..	$(CO)''(NH_2)(OH)$	Not known in a free state, but as an ammonia salt, which when heated forms ammonic carbonate and urea. It forms acid and neutral ethers.
	Carbimide ..	$(CO)''(NH)''$	Corresponds to cyanic acid.
	Carbamide ..	$(CO)''(NH_2)_2$	Corresponds to urea.

III.—Amides of the Triatomic Acids.

Ammonia salts of malic acid $(C_4H_3O_2)'''(OH)_3$	Malamic acid ..	$(C_4H_3O_2)'''(NH_2)(OH)_2$	Not known in the free state.
	Malimide (?) ..	(?)	
	Malamide ..	$(C_4H_3O_2)'''(NH_2)_2(OH)$	Metameric with asparagin.
Ammonia salts of citric acid $(C_6H_5O_4)'''(HO)_3$	Citramic acid ..	(?)	
	Citrimide.. ..	(?)	
	Citramide ..	$(C_6H_5O_4)'''(NH_2)_3$	

A nitrile is an ammonia derivative, where the three hydrogen atoms are replaced by a trivalent radical.

Thus the cyanides of univalent alcohol radicals may also be regarded as nitriles; for example:—

Hydrocyanic acid	CHN	=	(CH)N	formonitrile.
Methylic cyanide	$CH_3.CN$	=	$(C_2H_3)'''N$	acetonitrile.
Ethylic cyanide	$C_2H_5.CN$	=	$(C_3H_5)'''N$	propionitrile.
Phenyl cyanide	$C_6H_5.CN$	=	$(C_7H_5)'''N$	benzonitrile.

The term "nitrile" is applied to all bodies similar to those obtained by the abstraction of two molecules of water from ammoniacal salts, and which are capable of being again reconverted into the ammonia salt. Thus, if ammonic benzoate be distilled with anhydrous phosphoric acid, it furnishes benzonitrile,

$(NH_4)C_7H_5O$	=	$(C_7H_5)'''N$	+	$2H_2O$.
Ammonic benzoate	=	Benzonitrile	+	Water.

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whilst ammonic benzoate is re-formed on boiling benzonitrile with dilute acids or alkalies.

By the action of fuming sulphuric acid, the nitriles yield sulpho-acids. Thus benzonitrile yields sulphobenzoic acid—

$$(C_6H_4(HSO_3)CO_2H).$$

By the action of potassic hydrate, the nitriles yield ammonia and a salt of the corresponding acid containing the same number of carbon atoms. Thus:—

$(C_7H_5)'''N$	+	KHO	+	H_2O	=	NH_3	+	$KC_7H_5O_2$
Benzo-nitrile	+	Potassic hydrate	+	Water	=	Ammonia	+	Potassic benzoate.

This last reaction is important, inasmuch as certain cyanides or nitriles have been obtained, which, under the influence of hydrating agents, yield, instead of ammonia and the corresponding acid, an amine (or alcoholic ammonia) and formic acid. These are known as *isocyanides* and *carbamines*. For example: by the action of chloroform on aniline we obtain phenyl isocyanide, a body isomeric with benzonitrile. Thus:—

C_6H_7N	+	$CHCl_3$	=	$3HCl$	+	$C_7H_5N.$
Aniline	+	Chloroform	=	Hydrochloric acid	+	Phenyl isocyanide.

(*a.*) But *phenyl isocyanide*, when boiled with a dilute acid, yields formic acid and aniline. Thus:—

C_7H_5N	+	$2H_2O$	=	$(C_6H_7)'''N$	+	CH_2O_2
Phenyl isocyanide	+	Water	=	Aniline	+	Formic acid.

(*β.*) Whereas *benzonitrile* yields benzoic acid and ammonia. Thus:—

C_7H_5N	+	$2H_2O$	=	NH_3	+	$C_7H_6O_2$
Benzo-nitrile	+	Water	=	Ammonia	+	Benzoic acid.

The isocyanides are unaffected by alkalies, whilst the nitriles are easily decomposed.

Tests for Certain of the Alkaloids.

I. Alkaloids of Vegetable Origin.

Nicotine.—1. Tobacco odor. Turns brown by exposure.

2. *Solubility.* Soluble in water, alcohol, ether, and in the fixed oils.

3. *Heat.* Volatile.

4. *Auric and platinic chlorides* give precipitates.

Does not coagulate albumen.

Conine.—1. Odor of mice.

2. *Solubility.* Soluble in ether and alcohol; almost insoluble in water.

3. *Heat.* Volatile.

4. *Auric chloride* (but not $PtCl_4$) gives a precipitate.

Coagulates albumen.

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Quinine.—1. Crystals; tufts of needles. Solutions of quinine salts are fluorescent.

2. *Solubility.* Soluble in alcohol, ether, etc.; slightly soluble in water.

3. *Heat.* (1.) Entirely dissipated and decomposed when heated on platinum foil. (2.) Gives a violet-red sublimate, with quinoline odor, when heated in a test-tube.

4. *Sulphuric acid* dissolves it. The color produced is a faint yellow. (Salicine gives a red.)

Nitric acid dissolves it; no color, but turns yellow when heated.

Chlorine water and ammonia; a bright green solution.

Chlorine water, potassic ferrocyanide, and ammonia; a deep evanescent red solution.

5. Turns the plane of polarization to the *left.*

Cinchonine.—1. Crystals; four-sided prisms. Solutions of cinchonine salts are not fluorescent.

2. *Solubility.* Soluble in alcohol; very slightly soluble in water; insoluble in ether.

3. *Heat.* Similar to quinine.

4. *Chlorine water and ammonia*; a yellowish white precipitate.

5. Turns the plane of polarization to the *right.*

Morphia.—1. Crystals; four-sided prisms. Taste, bitter.

2. *Solubility.* Soluble in water and alcohol; insoluble in ether.

3. *Heat.* Melts, inflames like resin, leaving a little charcoal, which soon burns away.

4. *Nitric acid* turns it red; color destroyed by $SnCl_2$ and $(NH_4)_2S$. (*See* Brucia.)

Sulphuric acid dissolves it; solution colorless.

Ferric chloride (Fe_2Cl_6 neutral); colors it blue.

Narcotine.—1. Crystals; rhombic prisms.

2. *Solubility.* Insoluble in water; soluble in alcohol and ether.

3. *Heat.* Fuses and is finally dissipated.

4. *Sulphuric acid.* A red color when heated.

Chlorine water and ammonia; a yellowish-red liquid.

Atropine.—1. Crystals; silky needles.

2. *Solubility.* Slightly soluble in water and ether; soluble in alcohol and chloroform.

3. *Heat.* Fuses at 194° F., decomposes and partially sublimes.

4. *Auric chloride;* a yellow precipitate.

Aconitine.—1. Crystals not well marked. When a minute particle is placed on the tongue, it produces tingling and numbness.

2. *Solubility.* Slightly soluble in cold water, soluble in alcohol and ether.

3. *Phosphoric acid;* a violet tint.

Sulphuric acid turns it yellow, changing to a dirty violet.

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Strychnine.—1. Crystals; octahedra. Taste intensely bitter.

2. *Solubility.* Soluble in chloroform and methylic alcohol; slightly soluble in water and dilute alcohol; insoluble in absolute alcohol or ether.

3. *Heat.* Slightly volatile.

4. *Sulphuric acid* dissolves it without change of color; on adding MnO_2 or PbO_2, etc., to the acid solution, a play of color from purple violet to red is obtained.

5. The physiological test on a frog is infinitely the most delicate.

Brucia.—1. Crystals; needles arranged in stars.

2. *Solubility.* Soluble in water and alcohol; insoluble in ether.

3. *Nitric acid.* A bright red; becoming yellow by heat; violet by $SnCl_2$ or $(NH_4)_2S$. (*See* Morphia.)

4. *Chlorine water.* A red solution, becoming yellow with ammonia.

Caffeine.—1. Crystals; silky needles. Taste very bitter.

2. *Solubility.* Soluble in water, alcohol and ether.

3. *Heat.* Melts and sublimes.

4. *Nitric acid.* Solution red when evaporated to dryness; turns purple on adding ammonia.

II. Alkaloid of Animal Origin.

Urea.—1. Crystals; four-sided prisms permanent in air.

2. *Solubility.* Soluble in water and alcohol; insoluble in ether.

3. *Heat.* Evolves NH_3; partially sublimes.

4. *Nitric acid.* Forms crystals of nitrate of urea.

Potassic hydrate and heat; evolves ammonia.

Oxalic acid; deposits tabular crystals.

III. Artificial Alkaloid.

Aniline.—1. Liquid, with fragrant odor, becoming brown on exposure.

2. *Solubility.* Slightly soluble in water; very soluble in alcohol and ether.

3. *Heat.* Volatile.

4. *Alkaline hypochlorite* (chloride of lime); a purple color.

Heated with *mercuric chloride,* and the residue dissolved in alcohol forms a magenta solution. A solution in dilute sulphuric acid submitted to electrolysis turns blue (changing to violet) at the positive pole by the action of the nascent oxygen.

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CHAPTER XXIX.

COLORING MATTERS.

Natural History—General Preparation and Properties—Yellows—Reds—Blues—Browns—Blacks.

SUPPLEMENTARY CHAPTER: Dyeing and Calico Printing.

Natural History.—A few coloring bodies are found (1) in the *animal* kingdom, such as cochineal and sepia, but they occur almost entirely (2) in the *vegetable* kingdom.

Preparation.—(1.) By solution in water, spirit, ether, or oils.

(2.) By fermentation (*e.g.*, indigo, madder, archil, and litmus).

Preparation of Indigo.—The leaves of plants of the species indigofera, are placed in water and allowed to ferment. A yellow soluble substance is first formed, which in time turns blue, and becomes insoluble. This constitutes, when dried, the indigo of commerce. The change of color is due to the oxidation of a body existing in the plant, called *indican.*

Preparation of Madder.—Madder is prepared by a similar method of fermentation, whereby a yellow substance present in the plant, called *rubian* ($C_{28}H_{34}O_{15}$), becomes converted into alizarine ($C_{14}H_8O_4$).

Preparation of Archil and Cudbear.—The plants are first digested with lime and water, and the clear filtered solution neutralized with hydrochloric acid. The white precipitate thus produced, consisting of one or more acids, such as erythric, evernic, and lecanoric acid, is dissolved in hot alcohol. This solution is then boiled with lime, by which means the acids are decomposed. The clear solution from which the excess of base has been removed, yields on evaporation and extraction with boiling alcohol, the colorless body called *orcine* ($C_7H_8O_2$), which by the action of air and ammonia forms the red coloring matter *orceine* ($C_7H_7NO_3$).

In practice, the *archil* and the *cudbear* are mixed with lime and urine (the latter to furnish ammonia), and exposed to the air for some weeks. In the case of *litmus*, ammonic and potassic carbonates are used instead of lime and urine. The red color produced in the case of litmus is *azolitmine* ($C_7H_{10}NO_5$), which differs from orceine in its insolubility in alcohol.

(3.) By artificial processes, such as indigo-blue, which is prepared from aceto-phenone, alizarin from anthracene, etc.

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Properties. — (*General*). — The organic coloring matters are solid bodies. Some of them are crystalline, such as alizarin, moritannic acid, hæmatoxylin, etc.

Their colors are bright; they have but little taste or odor.

Heat decomposes most of them. A few are volatile (*e.g.*, indigo, alizarine).

Light bleaches most of them, especially if the coloring matter be moistened with water.

They are mostly soluble in water, but are insoluble in alcohol or ether.

Strong acids generally decompose them, sulphuric acid charring, and nitric acid oxidizing them. Weak acids change the blues to reds. Cyanine, for example, is the blue coloring matter of certain flowers, and the flower is *blue* if its juice be neutral, but *red* if it be acid.

They are all bleached by chlorine, by sulphurous acid, by reducing agents, and generally also by the action of nascent oxygen.

Alkalies change the reds to greens or blues, and the yellows to browns.

The metallic oxides combine with many of them to form permanent compounds (as, *e.g.*, the lakes). Thus alumina, ferric oxide, and stannic oxide are used as mordants. Charcoal generally both absorbs and destroys the colors.

I. The Yellows.

1. *Annatto* (seeds of Bixa Orellana).—The coloring matter "bixine" is soluble in alkalies.

2. *Chrysammic Acid.*—Prepared by the action of nitric acid on aloes.

3. *Gamboge* (Hebradendron Gambogioides).—A gum resin, the coloring matter being soluble in water.

4. *Hœmatoxylin.* (Logwood; Hæmatoxylon Campechianum).—It forms the red *hæmatein* ($C_{16}H_{12}O_6$) in contact with oxygen and alkalies, and a black by the action of potassic chromate.

5. *Luteoline or Weld* (Reseda Luteola).—Soluble in water.

6. *Morindin* (Morinda Citrifolia) (*Soranjee*).

7. *Moritannic Acid* (Morus Tinctoria or Fustic).—Soluble in water.

8. *Oxypicric Acid.*—Prepared by the action of nitric acid on assafœtida.

9. *Phylloxanthin.*—Phylloxanthin is precipitated by boiling chlorophyll in an alcoholic solution of potash, and adding hydrochloric acid to the solution.

10. *Picric Acid* is a derivative of phenol, and also a product of the action of nitric acid on indigo.

11. *Purree or Indian Yellow* (origin ?).—A compound of magnesia and purreic or euxanthic acid.

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12. *Quercitrin* (Quercus Tinctoria).

13. *Rubian* (*See* Madder).

14. *Saffron* (Yellow Anthers of Crocus Sativus).—A glucoside.

15. *Turmeric* (Curcuma Longa).—The coloring matter *curcumine* is soluble in alcohol, but insoluble in water.

16. *Xanthin and Xantheine.*—The yellow coloring matter of flowers and of yellow leaves.

II. The Reds.

1. *Alizarin* (*See* Madder).

2. *Braziline.*—$C_{22}H_{20}O_7$, obtained from Brazil wood.

3. *Carmine; Cochineal;* (from insects of coccus tribe).—Cochineal is extracted by water and alcohol. The coloring body is *carminic acid* ($C_{14}H_{14}O_8$), which combines with alumina to form lakes.

4. *Draconine* (Dracœna Draco).

5. *Hæmetein* (*See* Hæmatoxylin).

6. *Madder Red* (Rubia Tinctorum).—By the fermentation of the yellow coloring matter *rubian* ($C_{28}H_{34}O_{15}$), whereby *alizarin* is formed ($C_{14}H_8O_4$).

7. *Orceine* ($C_7H_8O_2$).

8. *Safflower* (petals of Carthamus Tinctorius).—The coloring matter *carthamine* ($C_{14}H_{16}O_7$) is soluble in alkalies and is reprecipitated by acids.

9. *Santaline* (Pterocarpus Santalinus).

III. The Blues.

1. *Cyanine.*—This constitutes the blue colouring matter of flowers and also the colouring matter of grapes.

2. *Indigo* (various species of indigofera) (*See* General Preparation, page 677).—By the action of deoxidizing agents and an alkali, indigo becomes soluble and colorless (indigo white), changing to blue on exposure to air. Traces of indigo have been found in the urine.

Blue indigo	$C_{16}H_{10}N_2O_2$.
White indigo...	$C_{16}H_{12}N_2O_2$.

By oxidation, indigo forms *isatin* ($C_{16}H_{10}N_2O_4$), from which, by the action of chlorine, *chlorisatin* is derived ($C_{16}H_8Cl_2N_2O_4$).

3. *Litmus*, *Archil* and *Cudbear* (from various lichens, as Roccella Tinctoria (litmus), Lecanora Tartarea (cudbear)). These colors are developed by fermentation, whereby *orceine* ($C_7H_7NO_3$) is formed. (*See* General Preparation.)

4. *Phyllocyanine.*—From chlorophyll. This coloring matter remains in solution after the phylloxanthin has been precipitated.

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IV. The Greens.

1. *Chlorophyll.*—A resinoid body present in plants. It is soluble in ether, and consists of phylloxanthin (a yellow) and phyllocyanine (a blue).

V. Brown.

Sepia, from the cuttle fish.

VI. Black.

See Hæmatoxylin.
Pigmentum Nigrum.

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SUPPLEMENTARY CHAPTER.

DYEING AND CALICO-PRINTING.

Dyeing.—To obtain uniformity of color it is necessary that the coloring matter should be applied to the fabric in solution; but it is also essential, in order that the color should not be discharged when the fabric is washed, that it should be rendered insoluble in the fibre.

Sometimes the fibre itself forms an insoluble compound with the coloring matter. Thus, animal fabrics (such as silk and wool) combine with coloring matters; but if this does not happen, as in the case of cotton, other systems have to be adopted, such as the following:—(α.) The fibre is sometimes impregnated with a material called a mordant, such mordant being capable of forming an insoluble compound with the coloring matter (*e.g.*, alumina and cochineal). (β.) In the case of a color formed by the admixture of solutions, the fabric is first saturated with one solution and then dipped into the second, so that the insoluble coloring matter may be formed in the fabric itself. (Thus, a blue dye is formed from ferric chloride and potassic ferrocyanide.)

The *red dyes* used are madder and brazil wood, alum and bitartrate of potash being the mordants employed. Lac or cochineal are used for dyeing wool, stannic chloride and bitartrate of potash being used as mordants. The aniline colors are also employed, albumen being required as a mordant in dyeing cotton, no mordant being necessary for wool or silk.

The *blues* used in dyeing are usually *indigo*, the aniline blues, or prussian blue, the latter being formed by the admixture of solutions of ferric chloride and potassic ferrocyanide.

The *yellows* employed are weld, quercitron, fustic, annatto (aluminous mordants being used for each of these dyes), lead chromate (formed by the admixture of acetate of lead and potassic chromate), and carbazotic acid.

Browns and blacks are formed by a mixture of tannin and a salt of iron, different shades depending on the relative proportions of each, on the admixture of indigo, etc.

Calico printing.—This consists in the production of a pattern on the fabric. This is effected in different ways. (1.) By printing the pattern on the fabric with the mordant mixed with gum. By the action of water containing cow-dung (dunging) any excess of mor-

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dant is removed. The fabric is then dipped in the dye-bath, and any color except that on the mordanted pattern can be washed out with water. (2.) Sometimes a *resist* is used, that is, a substance, like citric or tartaric acid, which prevents the fabric taking the color on those parts to which the resist has been applied. (3.) Sometimes a *discharge* is used. The color from a uniformly printed fabric dyed with indigo, madder, etc., may be removed wherever desired by the application of an acid mixed with gum, and afterwards passing the fabric through a solution of chloride of lime. By this means the color will be discharged wherever the acid has been placed. Different colors may also be produced at the same time, by combining the acid with different reagents.

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CHAPTER XXX.

VEGETABLE CHEMISTRY.

Tissues of Vegetable—Cellulin—Vegetable Parchment—Gun Cotton—Woody and Corky Tissue—The Life of a Plant.

The organised structures of plants are made up of three kinds of material:—

(1.) *Cellulin* (*lignin*) $(C_6H_{10}O_5)_n$, which is the growing part of the plant, such as the cambium layer, etc.

(2.) *Woody matter* (*sclerogen*), such as the duramen or alburnum.

(3.) *Corky matter*, or the outer layer of the plant.

In the first of these three bodies, the hydrogen and oxygen are present in the proportion to form water, but in woody tissue and in corky matter the proportions are different.

I. Cellulin (*lignin; cellulose*) $(C_6H_{10}O_5)_n$. This constitutes the growing and the active part of the plant. It forms the basis of cells and the true cell-wall. In its purest form it is met with in the extremities of the roots and buds, in the pith or medulla, in the medullary rays, in the cambium or under layer of the bark, and in certain hairs or filaments about the seeds, such as cotton. Fungi and the substance called vegetable ivory are said to consist of nearly pure cellulin.

Preparation.—The adhesion of encrusting woody tissue to the cellulin is so great, that it is scarcely possible to prepare it in a state of absolute purity. By the consecutive action upon it of various solvents, such as water, alcohol, ether, dilute alkalies, and dilute acids, its *comparative* purity may be effected.

Properties.—(α.) *Physical.* A tasteless, colorless, and perfectly innutritious substance; specific gravity, 1·9. Its appearance varies. It is *spongy* in the shoots of germinating seeds; *porous* and *elastic* in the pith of the rush and elder; *flexible* and *tenacious* in the fibres of the hemp and flax; *compact* in the branches of growing trees; *hard* and *dense* in the shells of the filbert, etc. Cellulin possesses the power of depolarizing a ray of polarized light.

(β.) *Chemical.* Cellulin is insoluble either in hot or cold water, in alcohol, in ether, or in oils. It is soluble in an ammoniacal solution of cupric oxide, from which it may be precipitated by acids. It is not acted on by iodine. It is capable of fermentation, as shown in the ripening of fruits.

Concentrated alkaline solutions dissolve it slightly, converting it first into starch, and finally into gum;—hence fabrics are injured by being boiled in soda. Heated with alkalies it forms oxalic acid.

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Action of Acids.—Dilute mineral and organic acids have very little action upon it. Hydrochloric acid dissolves it when heated with it, the cellulin being precipitated on the addition of water. Sulphuric acid dissolves it, converting it first into dextrin, and finally, when boiled in a quantity of water, into glucose. Nitric acid (specific gravity, 1·2) has no action upon it unless heated, when it forms oxalic acid.

Vegetable Parchment.—*Preparation.* By immersing blotting-paper in a mixture of 2 parts of oil of vitriol and 1 part of water, with subsequent washing.

Properties.—Tough, waterproof, and transparent. It neither gains in weight nor alters in composition by the action of the acid, the change being purely molecular.

Gun-Cotton (Pyroxylin; cellulo-nitrin).—*Preparation.* By soaking cotton wool in a mixture of fuming nitric acid (1·5 specific gravity) and sulphuric acid.

$$C_6H_{10}O_5 + 3HNO_3 = C_6H_7(NO_2)_3O_5. + 3H_2O.$$
Cellulin + Nitric acid = Trinitro cellulin + Water.

Constitution.—Cellulin has been regarded as a trihydric alcohol, $C_6H_7O_2(OH)_3$, and pyroxylin as a nitric ether, $C_6H_7O_2(NO_3)_3$; the relationship existing between glycerin, $C_3H_5(OH)_3$ and nitro-glycerin $C_3H_5(NO_3)_3$, or between ethylic alcohol, $C_2H_5(OH)$ and ethylic nitrate $C_2H_5(NO_3)$ being of a similar nature. Its more rational formula, however, seems to be $C_6H_7(NO_2)_3O_5$, *i. e.*, regarding it as a substitution product of cellulin, $C_6H_{10}O_5$, where H_3 has been replaced by $(NO_2)_3$.

Properties.—(*a.*) *Physical.* The form and appearance of the cellulin remains unaltered by the action of the acid, nevertheless, it will be found to have increased 82 per cent. in weight, and to have lost its power of depolarizing a ray of light. It will be found, moreover, to have become hygroscopic and highly electrical when rubbed or pulled out briskly. It is insoluble in alcohol, water, ether and in dilute acids, but is soluble in acetic ether, in methylic acetate, and in a mixture of ether, ammonia, and potash.

(*β.*) *Chemical.* Its composition varies according to the strength of the acid used.

Thus, by using a less concentrated acid, less highly *nitrated* compounds may be produced, such as $C_6H_9(NO_2)O_5$ and $C_6H_8(NO_2)_2O_5$, the latter constituting the dinitro-cellulin used for collodion.

It inflames at or about 400° F. (204·5° C.).

By the action of reducing agents, such as nascent hydrogen, gun-cotton may be reconverted into cellulin.

The products of its combustion are CO, CO_2, N, HNO_3, and CN.

Collodion is a solution of dinitro-cellulin in a mixture of alcohol and ether.

Uses of Cellulin.—In *nature* its use is essentially vital, performing

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the functions of the plant, and elaborating the various products from the juice.

In the *arts* it is used in the manufacture of paper, cotton fabrics, gun-cotton, collodion, etc.

II. Woody Matter (*incrusting matter; Sclerogen*). This is the deposit found either within the cell, or encrusting the cell wall. It is difficult to obtain it pure on account of the rapidity with which it becomes oxidized. It is insoluble in water, alcohol, and ether. Unlike cellulin, it is soluble in alkalies. Exposed to the air, and more especially under the influence of parasitic plants, it becomes pulverulent, constituting "*dry rot.*" Sulphuric acid does not, as in the case of cellulin, convert it into sugar; nitric acid tinges it yellow, forming with it gelatinous compounds; hydrochloric acid renders it brown and black. Iodine and sulphuric acid change it blue. The products of its destructive distillation have been already described (page 501).

Uses.—In *nature* it gives support to the plant. In the *arts* its uses are numberless.

III. Corky Matter is also an incrusting matter, and is always found outside the cell wall. The entire plant—leaf, fruit, flower, and indeed every cell, is covered with it.

Properties.—It is lighter than and impermeable to water, and is insoluble in water, alcohol and ether. It is soluble in alkalies. It is insoluble in strong sulphuric acid except by heat, or after a long period of action, but it is soluble in nitric acid (specific gravity, 1·2), which changes it to suberic acid. It is dissolved by chlorine. It is turned brown (not blue) by iodine and sulphuric acid. It will not take a dye. These reactions show—

1. Why potatoes and fruits do not dry, *viz.*, owing to the impermeability of the corky matter to water.

2. Why cotton must be first bleached with chlorine before being dyed, *viz.*, to remove the corky matter present on the cells.

Uses in nature.—To bind the cells together, and also to prevent the moisture in the cells from evaporating.

The Life of a Plant.

The seed is placed in the ground.

The soil is formed by the combined action of air, and of rain containing carbonic acid in solution, upon, say, a granite rock. The water in the rock expanding in the act of freezing, assists in breaking down the rock upon which the rain and the air have previously acted. Thus the soil derives its *mineral* ingredients. Spores of the lower orders of plants, such as the lichens, find in this soil a resting-place, grow, live, and die; their remains supply the soil with the *organic* portion necessary for the growth of plants of a higher order.

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The seed is placed in this soil. Under the influence of warmth and moisture the *insoluble* starch of the seed, by the action upon it of a nitrogenized ferment (diastase), is converted into *soluble* sugar, capable of serving as the first food of the plant, until it is able to shift for itself. The germ shoots, that is, it sends forth leaves and roots. These are its two means of obtaining food, the former acting as lungs and the latter as mouths.

The food of the plant is entirely inorganic. One thing, however, is essential, *viz.*, that the food supplied to the plant should be soluble. The chemical action of the plant is an action of reduction or deoxidation.

The leaves inhale ammonia and water vapor, and also more particularly carbonic anhydride. Under the action of light they fix the carbon of the carbonic anhydride, and exhale pure oxygen.

The roots also take up—*carbon* as CO_2, derived from decaying organic matter, *nitrogen* from the ammonia carried down by the rain or the product of putrefaction, or derived from the nitrates and nitrites the results of nitrification, together with *sulphur*, *phosphorus*, and *chlorine* derived from the sulphates, phosphates, and chlorides of the soil.

Thus the plant grows. The tips of the buds and the extremities of the rootlets are the active points of growth. Here no starch is to be found, for all the starch in these parts is converted into sugar to aid the growth.

The culminating point in the life of the plant is the formation of its fruit. The unripe fruit contains an insoluble body called pectose, to which the hardness of unripe fruits is due, together with cellulin and an acid, such as citric, tartaric, malic, etc., to which their sour, rough and astringent taste is to be attributed. By the action of warmth, the acid and a peculiar ferment present in the fruit (*pectase*) react on the insoluble *pectose*, and change it into the soluble *pectin* of ripe fruits, which, as ripening proceeds, becomes transformed into pectic and pectosic acids. These impart to the juice its power of gelatinizing (that is, forming a jelly) when boiled. Further, the fruit as it ripens absorbs oxygen, and evolves carbonic acid. Thus the tartaric or other acids by oxidation are converted into fruit sugar. Thus—

$3C_4H_6O_6$	+	O_3	=	$C_6H_{12}O_6$	+	$3H_2O$	+	$6CO_2$.
Tartaric acid	+	Oxygen	=	Fruit sugar	+	Water	+	Carbonic anhydride.

whilst a similar change results in the case of the cellulin and of the starch by the assimilation of water.

Thus the ripe fruit becomes sweet and loses its sour taste.

The ripening action being complete, oxidation still continues, but it now induces the changes of decay and putrefaction.

Finally, the plant dies and decays. Its carbon is dissipated as CO_2, its hydrogen as H_2O, its nitrogen as NH_3. Thus the dead plant

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becomes the gaseous food for other and living plants, to be absorbed by their leaves. Its mineral constituents are washed into the soil, whilst its woody tissue rots and forms humus, which also serves as a source of food for vegetation.

The soil needs constant renewal in order to restore its exhausted fertility. This is effected by manuring; phosphorus, sulphur, nitrogen and silica, together with lime, magnesia, and the alkalies, are supplied by gypsum (which, as well as supplying lime and sulphur, serves to retain the carbonate of ammonia by converting it into sulphate), by bone-ash, by superphosphate, by sodic chloride (which may be converted into carbonate, silicate, or other salts of soda), by sodic nitrate, by the alkaline silicates (soluble silicates being needed more especially by the cereals), and by ammonic sulphate.

Further, dead plants, the ashes of plants, urine, solid animal excrement, guano (*i.e.*, the dung of carnivorous sea birds, which contains a large quantity of urate of ammonia), and soot which contains ammonia, are all employed as sources of food for the vegetable.

Sometimes the ground is allowed to lie fallow, chemical changes occurring by the action of air and moisture, whereby it becomes enriched.

The use of lime depends on its power of promoting the decay of organic, and the decomposition of mineral matters, whereby they are converted into soluble forms.

Lastly, it must be remembered that different plants, like different animals, need different foods. Hence the principle of "the rotation of crops."

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CHAPTER XXXI.

ANIMAL CHEMISTRY.

ALBUMINOIDS: I. Animal Solids — II. Nutrient Fluids — III. Digestion, and the Fluids concerned in it—IV. Excrementitious Products.

ALBUMINOIDS OR PROTEIDS.

These bodies form the chief part of the solid constituents of animal organs. They are also found in small quantities in vegetables.

The formula $C_{72}H_{112}N_{18}O_{22}S$ represents their composition approximately. They are all amorphous, and turn the plane of polarization to the left. They are insoluble in alcohol and in ether, but are soluble in water, in acetic and the mineral acids, and in the alkalies. They may be known by forming a yellow solution with nitric acid (xanthoproteic acid) which becomes orange-red when treated with ammonia. The caustic alkalies decompose them. They are precipitated from their solutions by acetic acid and by mercuric nitrate (Millon's reagent), leaving, in the latter case, a red supernatant solution.

According to Hoppe-Seyler, the albuminoids may be arranged as follows:—

Class I. Albumens.

(Soluble in water.)

Name.	Source.	Properties.
Ser-albumen..	Blood serum	A yellow elastic transparent body. Its aqueous solution is precipitated by alcohol. It is not precipitated by a small quantity of very dilute acid, but is precipitated by the addition of acids in large quantity. The precipitate is soluble in excess of strong HCl, and in strong HNO_3. When injected into the veins, it does not, like ov-albumen, pass into the urine.
Ov-albumen ..	Egg	Coagulated by ether and turpentine. It is insoluble in strong HNO_3. When injected into the veins, it passes into the urine unchanged.
Veget-albumen		Like ov-albumen.

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Class II. Globulins.

(Insoluble in water, but soluble in dilute acids and alkalies, and also in dilute solutions of NaCl or other neutral salts.)

Name.	Source.	Properties.
Myosin	Muscle	Coagulable by heat and by alcohol. It is soluble in very dilute HCl, rapidly becoming acid-albumen.
Globulin (paraglobulin).	Prepared from *Blood serum*, by passing CO_2 through a dilute solution. *Aqueous humour. Crystalline lens.*	The globulin from blood serum is *fibrino-plastic*, *i.e.*, it can form fibrin in contact with certain fluids (paraglobulin). In this respect it differs from the globulin of the crystalline lens (globulin). Precipitated by CO_2 or by very dilute acids from its solution in NaCl. Soluble in water saturated with oxygen, and in very dilute alkaline solutions; but if the solution contains 1 per cent. of alkali it dissolves as an albuminate, and not in a free state. It is converted into acid-albumen by dilute acids. It coagulates at 158° F. (70° C.).
Fibrinogen ..	Pericardial fluid. Hydrocele fluid, etc.	Produces fibrin when mixed with fibrino-plastic globulin (*fibrinogenous*). It is more difficult to precipitate by CO_2, and less difficult to precipitate by a mixture of alcohol and ether, than globulin.
Vitellin	Yelk of egg.	Vitellin is the residue left after treating the yelk with ether. It is a white granular body, insoluble in water, and soluble in solutions of neutral salts. It is neither fibrino-plastic nor fibrinogenous. It is converted into acid albumen by dilute acids, and is soluble in dilute alkalis as an albuminate.

Class III. Derived Albumens.

(Insoluble in water and in dilute NaCl solutions; soluble in dilute acids and alkalies.)

Acid albumen		If the albumens of Class I. be acted on with a small quantity of dilute acid (HCl or acetic), the coagulation of the albumen does not occur at 70° C., and its levo-rotatory action on a polarized ray is largely increased (acid albumen). On neutralizing the acid solution, a white precipitate of albumen is thrown down, which will now be found to be insoluble in water and in a NaCl solution, but soluble in an excess of alkali or of alkaline carbonates. Coagulates at 70° C. The albumens of Class II. are soluble in dilute acids as acid-albumen. The solution yields a precipitate when neutralized, which is not soluble in neutral saline solutions.
Alkali albumen or albuminate		Alkalies, like acids, prevent the coagulation of albumen (albuminates), the albumen being precipitated on neutralizing the solution.
Casein		Casein is closely allied to the artificial albuminates.

Class IV. Fibrin.

(Insoluble in water, and but slightly soluble in neutral saline solutions or in dilute acids and alkalies.)

Fibrin	Blood; lymph; chyle.	Believed to be formed by the contact of fibrino-plastic and fibrogenous substances (*see* Blood, page 699). Fibrin is very elastic and possesses a filamentous structure. It is insoluble in water, except at very high temperatures, or after a very lengthened action. It swells up when acted on with dilute acids and alkalis, and after their prolonged action, aided by heat, dissolves slightly.

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Class V. Coagulated Proteid.

(Insoluble either in dilute or strong acids, except acetic acid; soluble in the gastric fluid (pepsin) which converts it first into syntonin and finally into peptone.)

Name.	Source.	Properties.
		This body is produced by the action of heat or of alcohol on neutral solutions of albumen, fibrin, myosin, etc. Strong HCl and also ether convert ov-albumen into a coagulated form. Heat similarly converts the albuminates into a coagulated form, but the precipitate may be reconverted into the albuminate by potassic hydrate.

Class VI. Peptones.

(Bodies formed by the action of the gastric juice on albuminoids; soluble in water, insoluble in alcohol and ether.)

Peptones.	Stomach and small intestines only.	These bodies are highly diffusible. They are not precipitated by acids or alkalies.

REACTIONS OF THE PROTEIDS.

The following Table taken from Fownes' (Watt's) exhibits the reactions of the several proteids before named:—

Soluble in water:
- Aqueous solutions not coagulated by boiling, — PEPTONES.
- Aqueous solutions coagulated by boiling . — ALBUMENS.

Insoluble in water:
- Soluble in a 1 p. c. solution of sodic chloride, — GLOBULINS.
- Insoluble: „ „
  - Soluble in hydrochloric acid (0·1 p. c.) in the cold:
    - Soluble in hot spirit . . . . — ALKALI-ALBUMEN.
    - Insoluble in hot spirit . . . . — ACID-ALBUMEN.
  - Insoluble in hydrochloric acid (0·1 p. c.) in the cold:
    - Soluble in hydrochloric acid (0·1 p. c.) at 60° C. . . . . — FIBRIN.
    - Insoluble in hydrochloric acid (0·1 p. c.) at 60° C.; insoluble in strong acids:
      - Soluble in gastric juice . . . — COAGULATED ALBUMEN.
      - Insoluble in gastric juice . . . — AMYLOÏD.

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A.—ANIMAL SOLIDS.

BONES, TEETH, SHELLS, ETC. FLESH, GELATIN, CHONDRIN, HAIR, SILK, BRAIN AND NERVE TISSUE.

Bone, Teeth, Shells.

TABLE I.

Composition of the healthy human bones of a child and an adult:—

	Bones from a child æt. 13 months. Cause of death bronchitis.						Bones from a male æt. 40 years. Cause of death bronchitis.					
	Femur.	Tibia.	Fibula.	Humerus.	Radius.	Ulna.	Femur.	Tibia.	Fibula.	Humerus.	Radius.	Ulna.
Calcic phosphate and fluoride.	49·6	47·5	47·6	50·6	45·1	49·2	60·2	57·9	57·4	61·8	57·4	58·2
Calcic carbonate.	6·0	6·0	5·9	7·1	5·0	6·4	8·0	7·8	7·5	8·8	7·3	7·8
Magnesic phosphate.	1·0	0·8	0·8	1·0	1·0	0·8	1·4	1·4	1·3	1·4	1·3	1·6
Animal matters.	43·4	45·7	45·7	41·3	48·9	43·6	30·4	32·9	33·8	28·0	34·0	32·4

TABLE II.

Composition of the bones of different mammals, birds, fishes, and reptiles:—

	Mammals (Femur of).							Birds (Femur of).		Fishes (Vertebræ of.)		Reptile (Femur)
	Human æt. 40.	Sheep æt. 4.	Bull æt. 4.	Horse æt. 6.	Wild Boar.	Wolf.	Bat.	Thrush.	Sparrow.	Cod.	Salmon.	Rana Esculenta.
Calcic phosphate.	58·0	55·9	54·1	54·4	58·9	57·9	57·5	58·6	59·5	57·6	36·6	59·5
Calcic fluoride.	2·2											
Calcic carbonate.	8·0	12·2	12·7	12·0	9·0	11·1	4·8	5·1	8·9	4·9	1·0	2·2
Magnesic phosphate.	1·4	1·0	1·4	1·9	1·2	1·1	1·0	0·8	1·0	2·3	0·7	1·0
Other salts.	..	0·5	0·8	0·7	0·9	1·0	0·7	0·8	0·9	1·0	0·8	1·8
Animal matters.	30·4	30·4	31·0	31·0	30·0	28·9	36·0	34·7	29·7	34·2	60·9	35·5

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Table III.

Composition of certain diseased bones, of teeth, and of various shells :—

	Diseased Bone.		Tooth.	Enamel of Tooth.	Crab Shell.	Oyster Shell.	Hen's Egg Shell.	Fish Scales (Perch).
	Rachitis. Tibia.	Caries. Femur.						
Calcic phosphate .. / Calcic fluoride	26·9	38·4	64·3	88·5	6·0	1·2	1·0	37·8
Calcic carbonate ..	4·9	5·4	5·3	8·0	62·8	98·3	97·0	3·0
Magnesic phosphate	0·8	1·1	1·0	1·5	1·0	..	..	0·9
Other salts	1·1	0·9	1·4	..	1·6	..	..	..
Animal matter ..	66·3	54·2	28·0	2·0	28·6	0·5	2·0	57·4

Omitting the periosteum or external membrane of the bone and the internal membranes, marrow, etc., we may say that bone consists of a mixture of an organic substance, called ossein, with inorganic compounds. It has been stated that iron has been found in bone, but if present, it is probably due to the retention of blood in the bone.

We would note that :—

(1.) There is a close resemblance in the chemical composition of the bones of the higher mammalia. (Table II.)

(2.) The bones of the young contain more animal matter, and less earthy matter than the bones of adults. There is, however, no well-marked gradation in the proportions. (Table I.)

(3.) The composition of bone is influenced by certain diseases. (Table III.) The alteration generally consists in a diminution of the earthy constituents.

(4.) The composition of bone varies slightly with the part from which it is derived. Thus the femur and humerus contain more earthy matter than the tibia and fibula or the radius and ulna, whilst the scapula, the sternum and the vertebræ contain less earthy matter than the long bones. (*See* Table I.)

(5.) It would seem that the bones of males contain slightly more earthy matter than the bones of females.

(6.) Of other animal substances closely allied to bone we note—

(α.) **Teeth** (Table III.). The substance of the teeth is (excepting the enamel) very like bone in its composition. The enamel (*i.e.* the covering of the tooth external to the gum), is remarkable for containing very little organic matter and a large excess of inorganic constituents.

(β.) **The Shells** of the crustaceæ, and of the mollusca, and also birds' eggs, contain generally but little phosphate and a considerable excess of carbonate of lime.

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(γ.) In **Fish Scales** the phosphate of lime is less, and the animal matter more, than in bone.

Properties of bone.

(α.) *Action of heat in open vessels.* The organic matter burns away, leaving a white "bone-ash" ($Ca_3P_2O_8$). This residue is used in the manufacture of phosphorus (*see* page 124), and also as a manure, in the form principally of superphosphate.

(β.) *Action of heat in closed vessels* (destructive distillation). Ammonia and tarry matters (*Bone-oil* or *Dippel's oil*) are given off, the residue in the retort constituting "*Animal Charcoal*" or "*Bone black.*" This consists of a mixture of phosphate of lime and finely divided carbon. Animal charcoal is largely used by the sugar refiners. When its decolorizing power has been exhausted, it is burnt for the purpose of recovering the bone ash.

(γ.) *Action of water.* When bones are boiled in water at 212° F. (100° C.) all that occurs is the separation of the grease present in the bone. This floats on the surface of the water, the ossein of the bone being insoluble. If the bone, however, be digested in water at a temperature of 300° F., as in a Papin's digester, the organic matter is rapidly converted into gelatin, which is soluble in water. This converted ossein is used for glue.

(δ.) *Action of acids.* When dilute hydrochloric acid is added to bone, effervescence first occurs by its action on the lime carbonate. In time the dilute acid dissolves out the whole of the earthy phosphates, etc., leaving only the ossein (the organic constituent of the bone), a semi-transparent horn-like body, which by the action of heat under pressure is converted into gelatin.

(ε.) *Action of burial.* After long burial the organic matter of bone disappears, leaving only the inorganic constituents.

Flesh.

Composition of Flesh—

Water	78·0
Fibrin (with nerve tissue, blood-vessels, etc.).	17·0
Albumen	2·5
Other constituents of the juice	2·5
	100·0

Muscle contains about three-fourths its weight of water, one part of which is due to the blood present, and a second part to the "*juice of flesh*," as it is called, *i.e.*, an acid liquid containing kreatin, inosite, and certain salts, together with phosphoric, lactic, and butyric acids.

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Kreatine ($C_4H_9N_3O_2aq$), when boiled in an acid, loses water and becomes *kreatinine* ($C_4H_7N_3O$), a minute trace of which is found in urine. When boiled with alkalies, kreatin gains water and yields *urea* (CH_4N_2O) and *sarcosin* ($C_3H_7NO_2$).

Inosite or *muscle sugar* ($C_6H_{12}O_6.2aq$), a body similar in composition, but dissimilar in properties, to grape sugar, may be obtained from the concentrated extract of flesh. It may also be obtained from green kidney-beans.

As soda is the chief alkali of the blood, its alkalinity being supposed to be due to phosphate of soda (Na_2HPO_4), so potash is the chief alkali of the juice of flesh, its acidity being supposed to be due to the acid phosphate of potash (KH_2PO_4).

Gelatin and **Chondrin** do not pre-exist in the animal kingdom, but result from the action of boiling water on gelatinous tissues (such as skin, tendons and bones),* or on chondrin-producing tissues (such as the cartilages of the ribs and joints).

Ultimate Composition of Gelatin and Chondrin.

	Gelatin.	Chondrin.
Carbon	50·0	49·1
Hydrogen	6·6	7·1
Nitrogen	18·3	14·4
Oxygen	25·1	29·4
	100·0	100·0

In addition to the above, earthy phosphates are always present.

Gelatin is found in a pure state as isinglass (the dried swimming-bladder of the sturgeon), and in a less pure state as calf's-foot jelly, glue, and size. It is soluble in hot water, but insoluble either in cold water, in alcohol, or in ether. It shrinks greatly in bulk when exposed to dry air. When perfectly dry, gelatin may be preserved indefinitely, but when moist it rapidly becomes acid, and putrefies.

A gelatin solution is precipitated as tanno-gelatin by tannic acid† (the only acid known that possesses the power of precipitating it), by alcohol, by mercuric chloride, by mercurous and mercuric nitrates, and by chlorine (forming a chlorite of gelatine). It is neither precipitated by alum nor by basic or neutral lead acetate.

Boiled with strong alkaline solutions, it is converted into *leucine*, or *amido caproic acid* ($C_6H_{13}NO_2$), and *glycocol* (glycocine) or *amido-acetic acid* ($C_2H_5NO_2$), with the evolution of ammonia.

* The gelatin from bone is called ossein.

† Leather consists of a combination of a gelatinous tissue (as skin) with tannin (*see* page 637).

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A one per cent. solution sets on cooling. Repeated boiling destroys this property of gelatin.

Chondrin is the gelatin obtained by the action of boiling water on the cartilages of the ribs and joints.

It is not so soluble as gelatin in boiling water. It is precipitated by acids. In the case of acetic acid the precipitate is insoluble in an excess of acid, but in the case of the other acids the least excess of acid effects the solution of the precipitate. Its solution is precipitated by alum and by lead acetate. It forms glucose when boiled with hydrochloric acid.

Uses.—*Size* is the gelatinized solution produced by boiling clippings of hides, parchment, etc., in water.

Glue is manufactured by boiling the parings of hides, etc., in water. The hides are first carefully cleansed from hair and blood by lime. This done, the lime is carbonated by free exposure, after which the hides are boiled in water. The liquid is then kept warm for a time so as to allow the impurities to subside. The solution is then cooled, the gelatinized mass being cut into slices and dried on nets in the air. The temperature at which the drying process is effected is important, for a summer heat would melt the glue, whilst a winter cold would split it.

Hair contains 3 to 5 per cent. of sulphur.

Silk.—This is said to consist of three layers, the *outer* one being *gelatin*, and soluble in water; the *centre* one *albumen*, and soluble in boiling acetic acid; the *inner* one *sericin*, and insoluble either in water or in acetic acid.

Brain and Nerve Tissue.—The *watery* extract (75 to 80 per cent.) contains kreatin, uric acid, xanthin, sarcine, inosite and lactic acid; the *solid undissolved matter* consisting of protagen, cholesterin and albumen. The ash (3 to 4 per cent.) consists mainly of salts (especially potassium salts) of sulphuric and phosphoric acids.

B.—NUTRIENT ANIMAL FLUIDS.

BLOOD, CHYLE, LYMPH, MILK.

Blood.

Composition.—This can be only stated very generally, although it is to be remarked that the composition of blood is singularly uniform, considering the work it has to perform in supplying the materials for the replenishment of worn-out tissue, and the carrying away some of the products arising from their destruction.

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Average Composition per 1,000 *parts of Human Blood* (Becquerel and Rodier).

The quantities are stated in parts per 1,000 of blood.		Male.		Female.
Specific Gravity of defibrinated blood		1060·0		1057·5
Do. of serum		1028·0		1027·4
Water		779·00		791·10
Fibrin		2·20		2·20
Fatty matters.	Saponified fat	1·00		1·04
	Phosphorized fat	0·49		0·46
	Cholesterin	0·09		0·09
	Serolin	0·02		0·02
		1·60		1·61
Albumen		69·40		70·50
Blood corpuscles		141·10		127·20
Extractive matters and salts		6·80		7·40
		1,000·10		1,000·01
Salts	Sodic chloride	3·10		3·90
	Earthy phosphates	0·33		0·35
	Soluble salts other than NaCl	2·50		2·90
		5·93		7·15
Iron		0·57		0·54

It may be noted that arterial blood contains more fibrin and less fat and albumen than venous blood.

The gases present in blood have been estimated by Magnus and Meyer.

Free gases present in 100 *vols. of blood taken from the carotid of a dog.* (*Corrected to* 0° C. *and* 760 *mm.*)

	Exp. 1.	Exp. 2.
Oxygen (free or combined with hæmoglobin)	12·43	14·29
Nitrogen	2·83	5·04
Free carbonic anhydride	5·62	6·17
	20·88	25·50

The *combined* carbonic acid was found to be, in the first experiment, 28·61 volumes in 100 volumes of blood, and in the second experiment, 28·58 volumes. This would give a total of 49·49 and 54·08 volumes of gas, free and combined, in 100 volumes of blood. *Relatively*, venous blood contains more carbonic acid and less oxygen than arterial; but *absolutely*, the carbonic acid, in both arterial and venous blood, is always in excess of the oxygen.

Constitution.—Fresh blood, as revealed by the microscope, consists of numerous red globules (*blood corpuscles*) and a few colorless corpuscles, floating in a colorless liquid. This colorless liquid, termed

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the *liquor sanguinis*, consists of what is called the serum of blood, holding the fibrin in solution. The composition of the blood corpuscles and of the liquor sanguinis respectively, are stated in the following table:—

Average Composition per 1000 *parts of Blood Corpuscles and of Liquor Sanguinis (Serum and Fibrin).*

Blood Corpuscles [Sp. Gr. 1088·5].		Liquor Sanguinis [Sp. Gr. 1028].	
Water	688·00	Water	902·90
Solid constituents	312·00	Solid constituents	97·10
Consisting of—			
Globulin and cell membrane, or *stroma*	282·22	*Consisting of—*	
Hæmatin *(with iron)*. [This body is a derivative of hæmoglobin.]	16·75	Albumen	78·84
Fat	2·31	Fibrin	4·05
Extractive matters	2·60	Fat	1·72
Mineral matter *(without iron)*	8·12	Extractive matters	3·94
Consisting of—		Mineral matter	8·55
Chlorine	1·686	*Consisting of—*	
Sulphuric acid	0·066	Chlorine	3·644
Phosphoric acid	1·134	Sulphuric acid	0·115
Phosphate of lime ..	0·114	Phosphoric acid	0·191
,, magnesia	0·073	Phosphate of lime ..	0·311
Potassium	3·328	,, magnesia	0·222
Sodium	1·052	Potassium	0·323
Oxygen	0·667	Sodium	3·341
		Oxygen	0·403

I.—*The Blood considered generally.*

Properties.—(a.) *Sensible and Physical.* The blood is a viscid red fluid. As regards its *color*, we have already noted that this is dependent on the presence of red corpuscles, and not upon any coloring matter actually existing in a state of solution in the liquid portion or liquor sanguinis. The exact color of the blood varies:—

(1.) It differs according to its source. Thus: the blood in the arteries is florid red, that in the veins being dull purple. This difference of color was at one time supposed to be physical, and due to alterations in the capacity (dependent on change of shape) of the red corpuscles for reflecting and transmitting light. It is, no doubt, true that the more spherical the globules, or, in other words, the more swollen the corpuscles are with water, the darker colored is the blood. Hence it was taught that carbonic acid effected the expansion of the cells, thereby rendering them bi-convex, and the blood dark colored; whilst oxygen effected the contraction of the cells, thereby rendering them bi-concave, and the blood bright red. It is, however, tolerably evident that the color change is not simply physical but chemical,

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and dependent on the state of oxidation of the hæmoglobin, or blood-coloring matter. Thus, in arterial blood the hæmoglobin is oxidized, and of a scarlet color; whilst in venous blood a part of the hæmoglobin is deoxidized, and of a purple color. Possibly, the physical condition of the corpuscles, and also the presence of carbonic acid, may be elements in the case; nevertheless, there can be but little doubt that the change of color is primarily, if not entirely, due to the oxidation and deoxidation of the hæmoglobin.

(2.) The quantity of hæmoglobin in the corpuscles, as well as the proportion of corpuscles to serum, influences the color of the blood.

(3.) The form of the corpuscles (*see above*). Thus the more spherical the corpuscles, the darker the blood appears.

(4.) The thickness of the cell-wall of the corpuscles. Mulder supposed this to be the cause of the different colors of venous and arterial blood. He pointed out that potassic nitrate and iodide, and also sodic phosphate and carbonate, thicken the external membrane of the corpuscles, and render the blood of a lighter color.

(5.) Any reagents, like the caustic alkalis and certain organic acids, that burst the corpuscles, render the blood brownish-red.

The *odor* of blood is more marked when warm than when cold. By treating the blood with sulphuric acid, the odor becomes so apparent that it is often possible to say the animal from which the blood so treated was derived. (Barruel.) The odor is more intense and well marked in the blood of males than in that of females. It is supposed that this odor is due to a volatile fatty acid.

Specific Gravity. Normal blood has a specific gravity varying from 1052·0 to 1057·0. It is less in women, and especially in pregnant women, than in men, and least of all in children. The specific gravity of venous blood is always somewhat higher than that of arterial. The blood from various animals, so far as its specific gravity is concerned varies very little. The blood of the bullock (four experiments) was found to have a mean specific gravity of 1060·0, and that of the sheep (seven experiments), 1053·0. [Tidy.]

The *temperature* of the blood is usually 100° F. (37·8° C.), but the blood on the left side of the heart is said to be 1° to 2° F. (·55° to 1·1° C.) higher than the blood on the right side, whilst the blood is warmed by passing through the liver, and cooled by passing through the superficial capillaries.

(*β.*) *Chemical.* The blood has invariably a slightly alkaline reaction when first drawn from the body, but it becomes acid after a short time, owing, it is supposed, to the conversion of the sugar into lactic acid. Menstrual blood is said to be acid, but this is probably due to its intermixture with acid uterine or vaginal mucus.

Coagulation.—In from two to five minutes after the blood is drawn from the body it *coagulates*, and in seven to fourteen minutes the whole mass becomes gelatinous. This coagulation is due to the fibrin pre-

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sent in a *soluble* state in living blood, becoming insoluble in the dead blood. The cause of this change is not understood. It has been suggested that it is due to the contact of foreign matter with the blood when drawn from the body. (Lister.) Others suppose that the inherent tendency of the fibrin to coagulate, is prevented during life by some inhibitory power resident in the walls of the containing vessels. Others suppose that coagulation of the fibrin does take place in the body, but that the tissue needing it absorbs the coagulated mass as soon as formed. Others believe coagulation to be due to the escape of ammonia and carbonic acid when the blood is withdrawn from the body; whilst others hold (Schmidt and Buchanan) that fibrin is not present at all in living blood, but that coagulation results when the blood is drawn, from the actual formation of fibrin by the union of two substances existing separately in the fluid and living blood. The solid mass now gradually *contracts*, forcing out a watery fluid. This stage of contraction, [or the separation of the *clot* or *crassamentum*, which consists of fibrin with the blood corpuscles entangled in its meshes (the blood corpuscles not having had time to subside before coagulation) from the *serum*, which is the liquor sanguinis *minus* the fibrin and in which the clot floats,] is usually complete in from twelve to forty hours.

If, from any cause the fibrin contracts less rapidly than usual (as happens in inflammatory blood), or the red corpuscles sink more rapidly than usual, owing either to a greater tendency of the blood corpuscles to form rouleaux as in inflammation, or to a great relative deficiency of red corpuscles, as in chlorosis, a white layer collects on the surface of the clot, consisting either of fibrin only, or of a mixture of fibrin and white corpuscles. This constitutes what is called the "buffy coat," or the "inflammatory crust" of blood. This buffy coat contracts more rapidly than the rest of the clot. Hence a cupped depression on the surface of the clot becomes apparent after a short time.

Coagulation is influenced by a variety of circumstances:—

(1.) *The Origin of the Blood.*—Women's blood coagulates more rapidly than the blood of men, but the clot is less firm. Embryonic blood coagulates imperfectly. Arterial blood coagulates more rapidly than venous.

(2.) A warmth of 100° to 120° F. (37·8° to 48·9° C.) promotes coagulation. A higher temperature than this retards it, whilst a temperature of 200° F. (93·3° C.) stops coagulation altogether, even after the blood has been cooled. Conversely, a cold of 40° F. (4·5° C.) entirely stops coagulation; but coagulation will, under these circumstances, take place as well as ever after the normal temperature of the blood has been restored.

(3.) Motion retards coagulation, but rest promotes it.

(4.) The multiplication of points of contact promotes coagulation.

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Thus we whip blood with a bundle of twigs to coagulate the fibrin. Or, again, the blood coagulates more rapidly in the rough cavities of the heart than in the smooth veins and arteries.

(5.) Contact with living tissue retards coagulation, whilst contact with foreign or dead tissue favours it. Thus we pass a thread through an aneurism to form a nucleus for coagulation, and to assist the cure.

(6.) The addition of two parts of water to one of blood promotes coagulation, but the admixture of a greater quantity of water retards it.

(7.) Free access of air promotes, whilst exclusion of air retards coagulation.

(8.) Coagulation is either retarded, or entirely prevented, by the alkaline hydrates, carbonates, and acetates; also by dilute acids; also by potassic or calcic nitrates, by ammonic chloride, etc.

(9.) Coagulation is influenced by the mode of death. Thus in death by asphyxia, where the blood is imperfectly aërated, coagulation is retarded. According to Hunter, the same result occurs in death from lightning, blows on the stomach, over-exertion, fits of anger, etc.

(10.) The consistency of the clot depends chiefly on the quantity of fibrin present in the blood.

The blood consists, as we have said, of corpuscles and serum, in the following proportion, according to Schmidt, per 1,000 parts:—

	Man.	Woman.	Dog.
Moist corpuscles	513·02	396·24	543·56
Serum	486·98	603·76	456·44

II.—*The Blood Corpuscles.*

The composition of the blood corpuscles has been already stated (page 967). These corpuscles are of two kinds, red and white.

1. *The White Corpuscles.*—These are present in blood in the proportion, in health, of 1 white to 400 or 500 red. This proportion, however, is greatly influenced, (α.) *by food*, the quantity of white corpuscles being decreased by fasting, increasing in number half an hour after food has been taken, the increase continuing, on an average, for two hours. (β.) Their proportion again is influenced *by disease*, the quantity being increased in pneumonia, tuberculosis, and more especially in leucocythemia. (γ.) Moreover, in the blood of certain portions of the body, as in splenic blood, their relative proportion is greater.

The white corpuscles are circular and nearly spherical. They have the power of assuming various irregular forms, known as their

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"amæboid movements." They are about $\frac{1}{2500}$ of an inch in diameter. They are specifically lighter than the red corpuscles. They contain neither fat nor hæmoglobin.

2. *The Red Corpuscles.*—These are red, circular, flattened discs, having an average diameter of $\frac{1}{1000}$ of an inch, and an average thickness of $\frac{1}{10000}$ of an inch. To these corpuscles the red color of the blood is due, their relative proportion to the liquor sanguinis varying greatly under different circumstances. They are relatively fewer in women's blood than in men's, and fewer in the blood of the old and young of all animals than in that of the middle-aged. Moreover, their proportions vary in the blood of different animals; *e.g.*, there are relatively a greater number in the blood of birds than in the blood of carnivorous and herbivorous mammalia, whilst the proportion is smallest in the blood of cold-blooded animals. Lastly, the proportions vary in the blood of different vessels. Thus there are fewer in arterial than in venous blood, fewer in the portal vein than in the jugular, whilst they are most abundant of all in the hepatic. The quantity, moreover, in the blood is *diminished* by want of food, by repeated bleedings, and in certain diseases, such as diarrhœa, intermittent fever, chlorosis, affections of the brain, etc. The quantity is *increased* by a fat diet, and in such diseases as cholera, spinal irritation, the early stages of heart-disease, general plethora, etc.

Constitution and Properties of the Red Corpuscles.—The corpuscle is a non-nucleated body. It is not a cell, in the sense of a sac. It consists of a tough, elastic, transparent framework, or *stroma* (that is, not merely a cell-wall), infiltrated with a fluid containing globulin (an albuminous body), and a red coloring matter, called hæmoglobin. A little fatty matter, iron, and other mineral constituents are also present. The central light or dark spot seen with the microscope depends on the unequal refraction of the transmitted light.

The red corpuscles have an average specific gravity of 1·088, but this is influenced materially by disease. In a case of cholera, the corpuscles were found to have a specific gravity of 1·102. Inasmuch as the specific gravity of water is less than that of the fluid contents of the corpuscle, it follows that it will, when mixed with the corpuscles, pass by osmosis into the cell, thereby swelling, and finally, if the action be allowed to continue long enough, bursting it.

We now consider the chemistry of some of the constituents of the corpuscle.

1. Globulin is a substance similar in composition to, and in its properties closely resembling, albumen. It is found in large quantity (10 to 14 per cent.) in the crystalline lens, and for this reason is sometimes called *crystallin*.

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2. Hæmoglobin (*hæmato-globulin ; hæmato-crystallin*).—This is the true, and the only coloring matter of the blood of vertebrate animals. Its percentage composition is stated as—

Carbon	54·2
Hydrogen	7·2
Nitrogen	16·0
Oxygen	21·5
Sulphur	0·7
Iron	0·4 = 100·00

Preparation.—(1.) By the action of cold water, in which the hæmoglobin is soluble, on the corpuscles.

(2.) If a drop of blood, placed on a glass slide, be diluted with water, alcohol, or ether, and after a short exposure to air covered over with a thin glass slip, crystals of hæmoglobin will be apparent under the microscope. (Funke.)

Properties.—Hæmoglobin may be obtained from blood, with more or less ease, in a crystalline form (Hæmato-crystallin of Funke).

The forms of the crystals vary in different animals. Thus they are—

(α.) *Prismatic* in the blood of fish, in human blood, and in the blood of most mammals.

(β.) *Tetrahedral* in the blood of the rat, mouse, and guinea-pig.

(γ.) *Hexagonal* in the blood of the squirrel.

The formation of hæmoglobin crystals is promoted by light, and by the chemical action of oxygen and carbonic acid on the corpuscles. It is specially to be noted that the crystals are not the result of the evaporation of the water of the blood, inasmuch as they are formed more readily when the blood is diluted with twice its volume of water than when only mixed with one-half its volume.

Hæmoglobin is soluble in cold water, but not in hot. The prismatic crystals are soluble in 94 parts of cold water, the solution coagulating at 147·2° F. (64° C.), while the tetrahedral crystals are soluble in 600 parts of cold water, the solution coagulating at 145·4° F. (63° C.) This coagulation consists not only in the coagulation of the albumen, but in the formation of hæmatin. The red solution is decolorized by chlorine, with the precipitation of white flakes (the *chlorhæmatin* of Mulder), and is changed to a brownish-red color by carbonic oxide, and to a brown color by nitrogen. It may be said generally, that whatever precipitates hæmoglobin, destroys it. The feeblest acids (even CO_2) decompose it.

The remarkable property possessed by hæmoglobin of combining with and delivering up oxygen has been already referred to (*see* page 65).

Carbonic oxide displaces the oxygen of oxy-hæmoglobin to form a more stable compound with the hæmoglobin.

A body called *hæmatoidin* (*methæmoglobin* or *methæmatin*) ($C_{14}H_{18}N_2O_3$,

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Robin), is said to occur in blood after extravasation in the tissues of living animals, in the brown fluids of hydrocele, ovarian cysts, etc. It seems to be a body intermediate between hæmoglobin and hæmatin.

Hæmatin.—By the action of heat, or of mineral and other acids, and also of alkalies, etc., hæmoglobin is converted into *hæmatin* (*hæmatosin*) [$C_{68}H_{70}N_8Fe_2O_{11}$, Hoppe]. This body, which contains 12·8 per cent. of iron oxide, and was once supposed to be a constituent, and the true coloring matter of the red corpuscles, is now proved to be merely a product of the decomposition of the hæmoglobin.

Hæmatin is an amorphous, blackish-brown substance, without taste or odor. It is insoluble in water, alcohol, ether, acetic ether, in all oils, or even in the concentrated mineral acids; whilst it is soluble in alcohol acidulated with either sulphuric or hydrochloric acid, and in aqueous or alcoholic solutions of the alkalies or of their carbonates. The brown acid alcoholic solution, when treated with an alkali, appears red by reflected, and green by transmitted light. It is a body easy of reduction, but very difficult of oxidation. It is decomposed by chlorine, and by boiling with nitric acid.

Hæmatin Hydrochloride; Teichmann's *Hæmin Crystals; Blood Crystals.*

Preparation.—By acting on hæmoglobin with common salt and glacial acetic acid.

Properties.—Rhombic dichroic crystals, insoluble in water, alcohol, and ether, and soluble in acids and alkalies, but in acetic and hydrochloric acids only without decomposition.

III.—*The Liquor Sanguinis.*

The composition of the liquor sanguinis has been already stated (page 967). By the term "serum" is meant the liquor sanguinis, *minus* the fibrin.

Properties.—A straw-colored fluid in health, becoming, in certain diseases, such as icterus and pneumonia, of an intensely yellow color. Its average specific gravity is 1·028, and, in this respect, is singularly uniform. Its reaction is alkaline, the alkalinity being due to the presence of carbonate and phosphate of soda.

[NOTE.—Serum is also straw-colored and alkaline. It coagulates at 170° F. (76·1° C.).]

1. Water.—The quantity of water in blood varies. Thus there is more in the blood of women (especially during pregnancy) than in that of men, and more in those of advanced age than in the young. The proportion present is influenced by disease. Thus there is a great diminution in the quantity of water in the blood in cholera. And further, arterial blood contains more water than venous blood, whilst in both venous and arterial blood the actual proportion of

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water varies hourly with the food, exercise, and atmospheric changes. Nevertheless, a remarkable uniformity is noticeable, for that which lessens the water excites thirst; whilst, if an excess of water be added to the blood, the urine and sweat get rid of it.

2. Albumen ($C_{72}H_{112}N_{18}SO_{22}$). This varies from 60 to 70 parts per 1,000 of blood. It is the cause of the coagulation of the serum by heat. It may be obtained in a soluble state by evaporating the serum below 120° F. (48·9° C.), whilst, if the serum be evaporated at a higher temperature, the albumen becomes insoluble in water at ordinary pressures.

Hoppe considers that the albumen is not present in blood in a state of solution, but merely in a state of fine subdivision. Others believe it to be present as an albuminate of soda, whilst Enderlin believes it to be held in solution by the sodic phosphate. The blood of women contains more albumen than the blood of men, whilst arterial blood contains less albumen than venous. The quantity of albumen in the blood is decreased in such diseases as Bright's disease, scurvy, puerperal fever, etc., whilst it is increased in cholera, intermittent fever, etc.

A body called *vegetable albumen* is found in vegetable juices.

3. Fibrin.—The proportion of fibrin in blood varies between 2 and 3 parts in 1000. It is usually increased in inflammatory affections, as rheumatism, pneumonia, etc., and decreased in anæmic diseases, as typhus, chlorosis, etc. Its spontaneous and speedy coagulation distinguishes it from all analogous substances.

All muscular tissue consists of fibrin. The gluten of flour is often called vegetable fibrin, and bears a close resemblance to animal fibrin.

[For remarks on coagulation, *see* page 698.]

4. Fatty Matters.—The proportion of fat in blood is about 1·6 parts in 1000. The quantity is not increased beyond this amount by a fat diet, but is decreased by a want of fat food. Arterial blood contains less fat than venous, and the portal vein more fat than the jugular. The quantity of fat (and especially of cholesterin) is increased at the commencement of every acute disease, and also in some chronic diseases.

Most of the fatty matter present in the blood is in a saponified form. It would appear that the fats peculiar to various organs exist ready formed in the blood, as *e.g.* cholesterin (the fat of bile), cerebrin and the phosphorized fat of the brain, together with oleic, margaric and stearic acids, chiefly saponified, but also in a free state.

These fatty matters of the blood not only supply fat where it is needed, but serve by their oxidation to maintain the temperature of the body.

5. Extractive Matter.—This term includes *kreatin* and *kreatinine*, *glucose*, *urea*, *uric acid*, *hippuric* and *lactic acids*, and certain other bodies.

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Alcohol is said to be always present in blood in minute quantity, and is supposed to be formed by the fermentation of the sugar. (Ford. Jahresb., 1861, page 792.)

6. Mineral Matters.—The percentage composition of the ash of the serum may be thus stated:—

Sodic chloride	61·08
Potassic chloride	4·08
Sodic carbonate (Na_2CO_3)	28·87
Hydric sodic phosphate (Na_2HPO_4) ...	3·19
Potassic sulphate...	2·78 = 100·00

The proportion of mineral ingredients is greater in the blood of adults than in that of the young, greater in arterial than in venous blood, and greater in the serum of the portal vein than in that of the jugular. The quantity is influenced by diet and by disease. There is a larger quantity present in the blood of the cat, goat, and sheep than in the blood of men, birds, and pigs, whilst a smaller quantity is found in the blood of dogs and rabbits than in other animals.

The iron (a never failing constituent of blood) belongs exclusively to the red corpuscles.

[For many details connected with blood, such as the measurements of the corpuscles, tests, etc., *see* the Author's and Dr. Woodman's "Handybook of Forensic Medicine."]

Chyle and Lymph.

Chyle is the fluid of the *lacteals*, the lymphatics of the intestines. It is transparent during fasting, but milk-like during digestion. This milkiness is due to the presence of minute fatty particles termed the molecular base of the chyle.

Lymph is the fluid of the lymphatics. It is a clear, colorless, faintly alkaline, albuminous liquid, having no fatty particles such as occur in chyle in suspension.

In both lymph and chyle the presence of certain corpuscles may be perceived under the microscope.

Percentage Composition of Lymph and Chyle (Owen Rees).

	Lymph.	Chyle.
Water	90·237	96·536
Albumen	3 516	1·200
Fibrin	0·370	0·120
Animal extractive ...	1·565	1·559
Fatty matter ...	3·601	A trace
Salts...	0·711	0·585
	100·000	100·000

We remark — (1.) That lymph and chyle are substantially alike, except that chyle contains fat, and lymph none or nearly none.

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(2.) Lymph and chyle are substantially like blood, the difference being only one of degree. In fact these liquids probably are rudimental blood, containing corpuscles in process of development into red corpuscles. The difference between the lymph and chyle and the blood becomes less and less as the two former pass through the thoracic duct, or in other words as they approach the place where they are to be mingled with the blood.

(3.) Blood, lymph and chyle agree, in that they contain fibrin, and coagulate spontaneously, although the clot of lymph and chyle is softer than that of blood. Moreover in this property of spontaneous coagulation they differ from all other animal fluids.

Milk.

Milk is a liquid secreted by the female mammary gland after parturition. Microscopically it consists of fat globules, surrounded by an albuminous envelope, having a diameter of 0·0014 in., floating in a perfectly transparent liquid.

Composition per 100 *parts of human milk compared with that of the cow.* (Tidy).

	Woman's Milk.			Cow's Milk.
	Max.	Min.	Average.	Average.
Casein	4·36	2·97	3·52	3·64
Butter	5·18	4·45	4·02	3·55
Sugar of milk	4·43	3·29	4·27	4·70
Various salts	0·23	0·38	0·28	0·81
Total solids	14·20	11·09	12·09	12·70
Water	85·80	88·91	87·91	87·30
Total	100·00	100·00	100·00	100·00

Milk is a model diet. The casein is its azotized portion, whilst fat, sugar, and the mineral ingredients of food (of which the chief is phosphate of lime) are duly represented.

An increased yield of milk is promoted up to a point by an increase in the quantity of albuminous and fatty elements taken as food, and *vice versâ*. A very fat diet increases the proportion of all the ingredients and not of the fat only.

Milk is a yellowish, sweet liquid. The cream after a short time collects on the surface, the lower part or the skimmed milk increasing at the same time in specific gravity. If the cream be well agitated the albuminous envelopes burst, and the fat globules coalesce to form butter.

The reaction of fresh milk is variously stated. It is probably nearly neutral or very slightly alkaline, owing to the soda holding the casein

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in solution (albuminate). After a time the milk becomes acid and then coagulates. This action is rapid if the weather be warm and the air electrical. It is occasioned by the conversion of the milk-sugar into lactic acid, under the influence of the nitrogenized body casein, which acid effects the precipitation of the casein (lactic fermentation). This latter, containing the milk globules in mechanical admixture, constitutes "*curds*," and the clear liquid "*whey*."

Normal milk contains no albumen, but colostrum (that is, the first milk secreted after pregnancy) usually abounds in it.

Human milk has an average specific gravity of 1030.

C.—DIGESTION AND THE FLUIDS CONCERNED IN IT.

Saliva; Gastric Juice; Pancreatic Fluid; Bile; Intestinal Juice.

Digestion is a process of solution, *i.e.*, of rinsing or drenching the food with various secretions so as to extract from it the nutritious portions, and convey them into the circulation.

To carry out this rinsing process perfectly, the food is first, in most cases, cooked, and then chewed. In this way a perfect admixture of the materials with the various solutive agents is effected.

The following diagram represents the amount of the digestive fluids secreted daily, and the proportions of their chief constituents.

	Quantity Secreted.	Solid Matters.	Active Principles.
Saliva	3·53 lbs.	231 grs.	116 grs. of ptyalin.
Gastric juice	14·11 ,,	2,963 ,,	1,482 ,, of pepsin.
Pancreatic fluid ..	0·44 ,,	309 ,,	39 ,, of pancreatin.
Bile	3·53 ,,	1,234 ,,	1,058 ,, of organic ferment.
Intestinal mucus ..	0·44 ,,	46 ,,	28 ,, ,, ,,
Total	22·05 lbs.	4,783 grs.	2,723 grs. of special solvents.

Saliva.

Saliva is a fluid secreted by various glands, such as the parotid, the submaxillary, the sublingual, etc. Two to three pints in the 24 hours may be taken as the average quantity secreted. The exact amount, however, varies considerably. The quantity is decreased by fasting, and increased by the stimulus of food in the mouth, or by the mere mental impression connected with the sight or even the thought of food.

Composition per 1000 *parts of Saliva* (Frerichs).

Water	994·1			
Solids	5·9	{	Organic	3·61
		{	Inorganic	2·29

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The organic constituents of saliva consist of an albuminoid substance called *ptyalin* (πτύω to spit) (which constitutes about one-fourth of the total solid matter of the saliva), together with fat, epithelium, etc. The ptyalin is said to be contained more largely in the saliva secreted by the submaxillary than by the other salivary glands. The inorganic constituents consist of the phosphates of lime, magnesia, and soda (the deposition of the earthy phosphates on the teeth by the action of the ammonia of the breath constituting what is called "tartar,") of alkaline chlorides and a small but an ever present quantity of potassic sulphocyanide, said to be increased when sulphur is taken internally.

Properties, &c.—Saliva is a clear, feebly alkaline fluid. Its specific gravity varies from 1002 to 1009. The alkalinity of the secretion from the parotid is said to be more marked than that from the other salivary glands. During digestion, moreover, its alkalinity is increased. In certain diseased conditions the saliva becomes distinctly acid.

The action of the saliva is twofold—

(α.) As a *mechanical agent* it acts as a lubricator, assisting mastication and deglutition.

(β.) As a *chemical agent* its action depends on the presence of the ferment body '*ptyalin*,' by which the insoluble starch is transformed into soluble dextrin and glucose. This conversion of the starch is retarded rather than promoted by the gastric juice. The saliva may also, being an alkaline fluid, assist in emulsifying the fat.

Gastric Juice.

The gastric juice is a fluid secreted from the glands of the stomach, under the influence of disturbing causes, such as the introduction of food and other mechanical irritants, and more especially by soluble irritants, such as salt, etc. The quantity secreted in the twenty-four hours is variously stated at from 10 to 20 pints.

Composition of Human Gastric Juice per 1,000 *parts.*

Water	994·4			
Solid constituents ...	5·6	{	Organic (pepsin) ...	3·2
		{	Inorganic	2·4

The salts present in the gastric fluid consist of calcic, sodic, and potassic chlorides, and earthy phosphates.

The two important constituents of the gastric fluid are the free acid and the pepsin.

(α.) As regards *the free acid*, some investigators maintain it to be lactic acid, and others hydrochloric acid. M. Verneuil states that he has found both acids present in a free state, the hydrochloric acid being 1·7 parts in 1,000, and the lactic acid in the proportion of 1 part of lactic to 9 parts of hydrochloric acid. The quantity of acid is

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increased by taking alcohol, and decreased by taking sugar. (*See* "Med. Examiner," Vol. i., p. 783, and Vol. ii., p. 254.)

The fact probably is, that both acids are usually present, the hydrochloric, as a rule, largely predominating. In some cases, moreover, the presence of acetic, phosphoric, and butyric acids has been clearly demonstrated.

(*β.*) *Pepsin* is an albuminoid body, soluble in water, and insoluble in alcohol. Its solution is precipitated by corrosive sublimate, by solutions of tannic acid and of lead salts, and by alcohol. When a solution of pepsin is boiled, its action as a solvent of albuminoid matter is destroyed.

Properties, etc.—The gastric juice is a clear, acid, odorless fluid. It has a specific gravity varying from 1002·2 to 1002·4. It is miscible with water. It coagulates albumen. Its action is powerfully antiseptic. Its solution does not become turbid on boiling.

The action of the gastric juice as a solvent of albuminoid matters, such as fibrin, coagulated albumen, etc., depends on the joint presence of the acid and of the albuminoid ferment-body pepsin. A certain temperature (100° F.), and a perfect admixture of the fluid and food, as, *e.g.*, by mastication of the food, by the muscular action of the stomach, etc., are also necessary conditions. Thus, after a time varying from two to six hours, complete chymification of the food is effected, the fibrinous and albuminous constituents being converted into different *peptones* or soluble forms of albumen, such as albumino-peptones, fibrino-peptones, gelatino-peptones, etc., all of which differ from common albumen, besides their solubility, in being neither coagulated by heat, acid, nor spirit, and in their capability of being dialysed (*albuminose* of Mialhe). The composition of the chyme depends, of course, largely on the food, but it has the general appearance of a thick fluid, consisting of a solid, undigested portion, suspended in a liquid of a more or less yellow color, and of a more or less disagreeable odor.

The gastric juice has no action on starch or fat.

The Pancreatic Fluid.

This fluid, which in many respects is like the saliva (but unlike it in containing no sulphocyanides), is the secretion of the pancreas, a gland closely resembling the salivary glands.

Composition of Pancreatic Fluid per 1,000 *parts* (Schmidt).

Water	980·45			
Solids	19·55	{	Organic (pancreatin)...	12·71
		{	Inorganic	6·84

Properties.—A colorless fluid; specific gravity, 1008 to 1009. Its reaction is usually stated as alkaline, but this, so far as the fresh

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fluid is concerned, is doubtful. Its action depends on the presence of an organic principle, called *pancreatin*, an albuminoid ferment-body, constituting two-thirds of its total solids. Its action is two-fold: (1.) it emulsifies fat, converting it into a milky liquid, thereby rendering it capable of absorption by the lacteals; and (2.) it converts starch into glucose, and so effects its solution. (Dobell.)

The Bile.

The bile is the fluid secreted from venous blood by the cells of the liver.

Average Composition per 1,000 *parts* (Frerichs).

Water	...	859·2		
Solids	...	140·8	Biliary acids combined with alkalies (Bilin)	91·5
			Fat	9·2
			Cholesterin	2·6
			Mucus and coloring matters ...	29·8
			Salts	7·7

The quantity of solid matter is greater in the bile of the young than in that of the old, and is in excess in such diseases as cholera, heart-disease impeding the circulation, etc., whilst it is less than normal in severe inflammations, diabetes, etc.

Bile consists essentially of (1) a resinoid matter, and (2) a coloring matter.

(1.) *Resinoid matter* (bilin). This consists of the soda or potash salts of two, or of one of two, acids, one of which contains sulphur and the other none—

(*a.*) Salts of *taurocholic acid* ($C_{26}H_{45}NSO_7$), which, by the action of alkalies, forms *taurine* ($C_2H_7NSO_3$) and a non-nitrogenous acid, called *cholic acid* ($C_{24}H_{40}O_5$). Thus:—

$C_{26}H_{45}NSO_7$	+	H_2O	=	$C_2H_7NSO_3$	+	$C_{24}H_{40}O_5$.
Taurocholic acid	+	Water	=	Taurine	+	Cholic acid.

Taurine may be prepared artificially by passing olefiant gas over sulphuric anhydride, neutralising the product dissolved in water with ammonia, evaporating to dryness, and heating the residue (*isethionate of ammonia*, $NH_3.H_2O.C_2H_4SO_3$), so as to expel a molecule of water.

(*β.*) Salts of *glycocholic acid* ($C_{26}H_{43}NO_6$), which, by the action of alkalies, forms *glycocine* ($C_2H_5NO_2$) and *cholic acid* ($C_{24}H_{40}O_5$). Thus:—

$C_{26}H_{43}NO_6$	+	H_2O	=	$C_2H_5NO_2$	+	$C_{24}H_{40}O_5$.
Glycocholic acid	+	Water	=	Glycocine	+	Cholic acid.

[Glycocholic acid gives, on adding sugar and H_2SO_4, a purple red (Pettenkofer's test).]

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In the dog, sodic taurocholate only is present; in the pig, sodic glycocholate only is present; in man, sheep, etc., the taurocholates are in excess over the glycocholates; whilst in the ox and in most fish, the glycocholates are in excess over the taurocholates.

Pig's bile also contains *hyocholic acid* ($C_{24}H_{40}O_4$), and goose bile *chenotaurocholic acid* ($C_{29}H_{49}NSO_6$).

(2.) The *coloring matter* of the bile is termed *cholochrome*. This is a mixture of a *green* pigment, insoluble in chloroform, called *biliverdin* ($C_{16}H_{20}N_2O_5$), and a *brown* pigment, soluble in chloroform, called *cholophæin*. Of this latter there are two modifications; viz., the red *bilirubin* ($C_8H_9NO_2$), and the brown *biliphæin*.

A blue coloring matter has also been described.

Properties.—Bile is a viscid, greenish-yellow, bitter fluid, without odor when fresh, but very offensive after it has become putrid. It has a specific gravity of 1020. It does not readily mix with water.

Its reaction is slightly alkaline. It putrefies rapidly, becoming acid, owing to the presence of mucus derived from the gall-bladder, the hepatic ducts, etc.

The action of the bile is involved in much obscurity: it does not convert starch into sugar like the saliva and pancreatic fluid (doubted by Wittich); it does not dissolve fibrin like the gastric juice; it does not emulsify fat, or at any rate to the same extent, as the secretion from the pancreas. Some regard the function of the bile as the medium, by direct excretion, for the separation of an excess of carbon and hydrogen from the blood, thereby effecting its purification. This is manifestly its purpose in intra-uterine life. Nevertheless, that it is more than a mere excrementitious fluid, and plays an actual part in digestion, there can be but little doubt. Some have suggested that its function is to emulsify fat; others, that it assists the absorption of fat by moistening the intestinal mucous membrane; others, that it neutralises the acid peptones from the stomach; others, that its antiseptic power prevents the decomposition of the food as it passes through the bowels; others, that it acts as a natural purgative by its stimulating effect on the intestines. As yet, however, our knowledge on these points is very imperfect.

Gall-stones consist sometimes of cholochrome, held together by mucus (*oriental bezoar stones*), but most often of cholesterin around a nucleus of cholochrome. Moreover, earthy carbonates and phosphates are generally present.

The Intestinal Juice.

The fluid secreted along the whole course of the small intestines has an alkaline reaction, and contains 3 to 4 per cent. of solid matter. It has a powerful action in assisting digestion, combining

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the activity and digestive power of all the other secretions. Starch, fat, and albuminous substances are thus equally affected by it.

D.—EXCREMENTITIOUS PRODUCTS.

Urine; Urinary Calculi; Fæces; Sweat; Mucus; Pus.

Urine.

The urine in all animals is the vehicle through and by which the body rids itself of used-up solid matter, and of the excess of water present in the blood. It is in short the great outlet for the nitrogen of effete azotized tissue.

About 60 ozs. may be taken as the average quantity of urine secreted by an adult male in 24 hours, but this is subject to great variation, depending on such causes as the quantity of fluid taken, the season of the year, and the relative activity of the skin, lungs, and alimentary canal.

Average Composition of Normal Urine, and average quantity of the various Constituents excreted in 24 hours (Kirkes).

	Constituents per 1,000 parts.	Average quantity excreted in 24 hours (adult male).
Water	967·000	.. 52·0 ozs.
Urea..	14·230	.. 512·4 grains
Uric acid	0·468	.. 8·5 ,,
Extractives, Pigment, Mucus	10·167	.. 161·0 ,,
Salts	8·135	.. 425·0 ,,
Silica..	traces	.. traces.
	100·000	

(1.) The composition and character of the urine of different animals varies. Thus, in the *carnivora*, the urine is usually clear and acid, containing much urea, and but little uric acid. In the *herbivora*, it is usually turbid and alkaline, containing urea like the carnivora, together with a great excess of hippuric acid, but no uric acid; it also contains an abundance of the earthy carbonates (hence its turbidity), and but very little of the earthy phosphates, these latter being proportionately abundant in the fæces.

Carnivorous birds excrete urea in small quantities, but uric acid in abundance, whilst *granivorous birds* excrete uric acid in abundance, but no urea. *Serpents and other land carnivorous reptiles* secrete uric acid almost entirely, whilst *frogs and other amphibious reptiles* secrete urea, and mere traces only of uric acid. Even the insecta excrete uric acid.

Thus it would seem that in the animals that drink freely, the nitrogen is excreted as urea, whilst in those that drink but little, it is excreted as uric acid. It must be noted, however, that these differ-

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ences are differences for the most part of diet simply. For if a carnivorous animal (as a dog) be fed on a purely vegetable diet, or a herbivorous animal (as a rabbit) on a purely animal diet, a corresponding change in the urine results.

(2.) The composition of the urine varies greatly in disease. Thus the quantity of uric acid is increased in gout, etc.; albumen occurs in Bright's disease, etc.; sugar in diabetes, etc.

(3.) The composition varies hour by hour. The morning urine (*urina sanguinis*) consists chiefly of the products of tissue decomposition. Hence, our choice of this for analysis. The day and the evening urine is greatly influenced by the quantity and the character of the food ingested (*urina cibi* and *urina potûs*).

And here may be noted the changes that bodies undergo from the period of ingestion to that of urinary excretion—

(*a.*) The kidneys secrete certain bodies from the blood in an unaltered state, *e.g.*, many metals (such as As, Sb, Bi, Cu, Cr, Au, Fe, Li, Pb, Hg, Ag, Sn, Zn), free organic acids, alcohol (?), numerous salts, many of the alkaloids, such as morphia, strychnia, atropine, etc.

(*β.*) In other cases, the products secreted are oxidized products, or are otherwise changed. Thus, ammonia salts are converted into nitrates; sulphur, alkaline sulphides and sulphites, become sulphates; tannic becomes gallic acid. Or, again, the neutral salts of organic acids become carbonates; free iodine is excreted as an alkaline iodide; ferrocyanides become ferricyanides; indigo blue becomes indigo white; benzoic, cinnamic, and other acids are found in the urine as hippuric acid, etc.

Properties.—(*a.*) *Physical.* A clear yellow fluid, having a mean specific gravity in health of 1020. Its *color*, however, may vary even in health from a colorless liquid to a deep orange. In its *specific gravity*, variations occur in health ranging from 1015 to 1025, depending on the season of the year, diet, exercise, etc. In disease the variation is much greater, being sometimes as low as 1004, as in albuminuria, or as high as 1060, as in diabetes. Of its relative *clearness* it is to be noted that in health it often becomes turbid on cooling, due to the deposition of phosphates. The cause of its peculiar *odor* has not been well made out. The odoriferous principle, whatever it may be, undergoes speedy change.

(*β.*) *Chemical.* Healthy urine is generally acid. The acidity of the 60 oz. voided in the 24 hours may be taken as equivalent to about the acidity of 30 grains of oxalic acid. This acidity, which is less during digestion (and, indeed, after a meal the urine may even be alkaline) and most marked during fasting, is due to the acid phosphate of sodium, and according to some observers, to certain free acids, such as lactic acid (?).

After a certain time, varying from a few days to two weeks, the

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urine becomes alkaline. This alkalinity is due to the urea becoming converted into carbonate of ammonia, crystals of triple phosphate, confervoid growths and vibriones occurring simultaneously in the urine. Indeed, this change may be so rapid that under certain morbid conditions, as in cases of retention, it takes place in the bladder itself, thus rendering the urine turbid and alkaline when voided. The urine may, however, under certain other conditions, be alkaline when secreted. This occurs when neutral alkaline salts of the vegetable acids have been administered in excess, the acid being destroyed in the process of respiration, whilst the alkali appears in the urine as a carbonate.

We now consider in detail the various constituents of the urine:—

1. Water.—This varies according to season, exercise, drink, condition of nervous system, etc. Thus it is increased in diabetes (especially in D. insipidus), and decreased in albuminuria, in febrile affections, and, in short, in any disease increasing the secretion of water by other channels.

2. Urea.—*Carbamide* [CH_4N_2O, or $CO(NH_2)_2$], (*see* page 514).—Urea constitutes nearly one-half of the total solid matter of the urine. It is the principal outlet for the effete or the excessive nitrogen from the system. The quantity excreted is greatest with an animal diet, and least with a vegetable, greater in males than in females, and greater in middle age than in youth or old age.

Constitution.—The molecular formula for urea is CH_4N_2O. It is commonly regarded as the amide of carbonic acid—that is, just as oxamide ($C_2H_4N_2O_2$) is derived from ammonic oxalate [$(NH_4)_2C_2O_4$] by the abstraction of two water molecules, so urea (CH_4N_2O) is derived from ammonic carbonate [$(NH_4)_2CO_3$].

Preparation.—(A.) *Preparation from urine.* (1.) Evaporate the urine to a syrup, and mix the concentrated liquid with an equal bulk of nitric acid. In this way a quantity of nitrate of urea will be formed ($CO(NH_2)_2HNO_3$). Dissolve this compound in boiling water, and treat the solution with baric carbonate, when pure urea remains in solution. Thus—

$$\underset{\text{Nitrate of Urea}}{2(CO(NH_2)_2HNO_3)} + \underset{\text{Baric carbonate}}{BaCO_3} = \underset{\text{Urea}}{CO(NH_2)_2} + \underset{\text{Baric nitrate}}{Ba(NO_3)_2} + \underset{\text{Carbonic anhydride}}{CO_2} + \underset{\text{Water.}}{H_2O}.$$

The clear filtrate is then to be evaporated to dryness, and the urea separated from the baric nitrate by hot alcohol.

(2.) It may also be prepared by forming an oxalate of urea by the action of oxalic acid on the concentrated urine. On adding chalk to a solution of this oxalate in boiling water, calcic oxalate is precipitated, and a solution of urea results, which may be purified by crystallisation.

(B.) By the action of heat on ammonic cyanate.

(C.) By the decomposition of ammonium carbamate.

(D.) Urea was the first organic body prepared artificially, as follows.

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A mixture of potassic ferrocyanide (56 parts) and manganic peroxide (28 parts) is heated to redness, when the following changes occur :—

K_4FeCy_6	+	O_9	=	$4KCyO$	+	$2CO_2$	+	N_2	+	FeO
Potassic ferrocyanide	+	Oxygen	=	Potassic cyanate	+	Carbonic anhydride	+	Nitrogen	+	Ferrous oxide.

The residue is now treated with cold water, and the clear filtrate containing the potassic cyanate is mixed with ammonic sulphate (41 parts). The solution is then evaporated to dryness, and the urea separated from the potassic sulphate by solution in hot alcohol :—

$2KCyO$	+	$(NH_4)_2SO_4$	=	K_2SO_4	+	$2CO(NH_2)_2$
Potassic cyanate	+	Ammonic sulphate	=	Potassic sulphate	+	Urea.

Properties.—A colorless, inodorous body, crystallizing in long-flattened prisms. It is soluble in spirit (1 in 5 at 50° F.), and very soluble in water (1 in 1 at 60° F.), the solution being neutral and permanent. Its rapid decomposition in the urine into ammonic carbonate, (to which the ammoniacal odor of putrid urine is due), depends on the mucus present in the urine. When heated it melts, and finally decomposes, evolving ammonia and ammonic cyanate, and leaving a residue of cyanuric acid. It forms salts with acids, such as the nitrate of urea [$CO(NH_2)_2.HNO_3$), an important compound, an account of its difficult solubility in nitric acid. When boiled with solutions of caustic alkalies (cold solutions being without action upon it), it is resolved into ammonia and an alkaline carbonate—a similar result occurring when urea is fused with the alkaline hydrates, or heated with water in a sealed tube. It combines with metallic oxides ; thus the compound $CO(NH_2)_2,2HgO$ is produced when mercuric oxide is added to a solution of urea in a potassic hydrate solution. Urea is decomposed by nitrous acid and by chlorine.

Compound ureas are formed by the replacement of the hydrogen of the urea by hydrocarbon groups. In *sulpho-urea*, sulphur takes the place of oxygen [$CS(NH_2)_2$].

3. Uric Acid ; *Lithic Acid* ($C_5N_4H_4O_3$).—This is present in the urine in combination with soda and ammonia, and is probably derived from the disintegrated elements of albuminous tissues. These salts of uric acid, being more soluble in warm than in cold water, are frequently deposited as the urine cools, a reaction occurring in certain deranged states where an excess of uric acid is present.

The quantity of uric acid in human urine is increased by an animal, and decreased by a vegetable diet. It is increased in certain morbid states of the system. It varies greatly in different animals. In the feline tribe uric acid is often entirely replaced by urea. In birds and serpents the urea is often entirely replaced by uric acid. This suggests the notion that although urea and uric acid may have different origins and different offices, nevertheless that each may do the work of the other.

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Urate of soda constitutes the chief constituent of the gouty concretions called "*chalk-stones.*"

Preparation.—It has never been prepared artificially.

A. *From urine.*—By adding HCl to the concentrated urine. The uric acid is precipitated in the form of hard red grains.

B. *From the excrement of serpents.*—This consists of acid ammonic urate. Dissolve the excrement by boiling in a solution of potassic hydrate; filter, and add hydrochloric acid to the filtrate, when the uric acid is precipitated as a white crystalline powder. "Guano" is an impure uric acid, and is formed by the partial decomposition of the excrement of sea birds.

Properties.—Uric acid is a tasteless, inodorous, and sparingly soluble body (1 in 10,000). It is insoluble in alcohol and ether, but is soluble in strong sulphuric acid. When heated in a retort, a black residue remains, cyanic acid, hydrocyanic acid, carbonic anhydride, and ammonic carbonate being evolved.

Uric acid is a dibasic acid. Fused with an alkaline hydrate, it yields an alkaline carbonate, cyanate, and cyanide. Mixed with nitric acid, it effervesces, and if the resulting solution be evaporated nearly to dryness, and after dilution, mixed with a slight excess of ammonia, the characteristic deep red tint of murexide ($C_8N_6H_8O_6$) is immediately produced.

With hydriodic acid and heat, it is resolved into glycocin, carbonic anhydride, and ammonia.

Some Products of the Oxidation of Uric Acid.

Name.	Formula.	Preparation and Properties.
Allantoïn	$C_4N_4H_6O_3$	*Preparation.*—(1.) From the allantoic fluid of fœtal calf. (2.) By boiling uric acid with water and peroxide of lead. *Properties.* — Transparent colorless crystals; soluble in 160 parts of cold water. Decomposed by boiling with mineral acids and caustic alkalies.
Alloxan	$C_4N_2H_2O_4$4aq	*Preparation.*—By the action of strong nitric acid on uric acid in the cold. *Properties.*—White crystals; very soluble in water; crystals become anhydrous at 150° C.; solution acid, and stains the skin red; decomposed by both oxidizing and reducing agents. Forms a deep blue compound when acted on with an alkali and a ferrous salt. Alloxan appears to be the intermediate stage in the conversion, by oxidation, of uric acid into urea. When alloxan is boiled with peroxide of lead, urea is formed— $(C_4N_2H_2O_4+2PbO_2+H_2O=CH_4N_2O+3CO_2+2PbO)$. Alloxan forms alloxantin by the action of sulphuretted hydrogen.
Alloxantin	$C_8N_4H_4O_7$3aq	*Preparation.*—(1.) By the action of hot dilute nitric acid on uric acid. (2.) By the action of reducing agents (as H_2S) on alloxan. *Properties.*—Colorless crystals. Soluble with difficulty in cold water, more soluble in hot. Becomes anhydrous at 150° C. Solution acid. Gives a violet precipitate with baryta water, and a black precipitate with $AgNO_3$.—Converted by oxidizing agents into alloxan. Boiled in water with peroxide of lead, it forms urea and plumbic carbonate. Decomposed by the prolonged action of H_2S into dialuric acid.

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Name.	Formula.	Preparation and Properties.
Alloxanic acid	$C_4N_2H_4O_5$	*Preparation.*—By the action of baryta water on a solution of alloxan. The Ba is to be separated by H_2SO_4. *Properties.*—A crystalline bibasic acid. The solution is acid, and decomposes carbonates. It dissolves Zn with the disengagement of hydrogen. The silver alloxanate is insoluble. On boiling in water alloxanic acid forms urea and mesoxalic acid ($C_3O_3(OH)_3$).
Mesoxalic acid	$C_3O_3(OH)_2$	*Preparation.*—(1.) By heating a solution of baric alloxanate to boiling. (2.) By adding a solution of alloxan to lead acetate, and decomposing the lead mesoxalate with H_2S. Urea is formed at the same time. *Properties.*—A crystalline acid. It resists heat. The silver mesoxalate is insoluble.
Parabanic acid	$C_3N_2H_2O_3$	*Preparation.*—By the action of moderately strong nitric acid on uric acid, or alloxan, with the aid of heat. *Properties.*—A crystalline acid. The solution neutralised with ammonia and boiled, yields an ammonium salt of oxaluric acid.
Thionuric acid	$C_4N_3H_5SO_6$	*Preparation.*—By the action of a sulphurous acid solution on a cold solution of alloxan, and afterwards boiling the mixture with ammonia and ammonic carbonate. The ammonic thionurate formed is to be converted into a lead salt, which is then decomposed with sulphuretted hydrogen. *Properties.*—By boiling the solution it is resolved into sulphuric acid and uramil.
Uramil	$C_4N_3H_5O_3$	*Preparation.*—By boiling a solution of ammonic thionurate with a slight excess of hydrochloric acid. *Properties.*—A white crystalline body. Its ammoniacal solution turns purple in air. It is decomposed into alloxan and ammonic nitrate by nitric acid, and forms pseudo-uric acid by the action of potassic cyanate.
Murexide (Purpurate of ammonia)	$C_8N_6H_8O_6$+aq	*Preparation.*—(1.) By heating dry alloxantin with ammonia. (2.) By boiling uramil and mercuric oxide in a weak solution of ammonia. *Properties.*—The crystals appear green by reflected, and purple red by transmitted light. It is insoluble in alcohol and ether. It is soluble in hot, but not very soluble in cold water. It is decomposed by mineral acids, a white body (murexan) being precipitated. It is soluble in KHO, the solution being purple red, and disappearing on boiling.
Dialuric acid	$C_4N_2H_4O_4$	*Preparation.*—By the long continued action of H_2S on a boiling solution of alloxan. It is the final product of the action of reducing agents on alloxan.
Oxaluric acid	$C_3N_2H_4O_4$	

4. Hippuric Acid ($C_9H_9NO_3$); *Benzamidacetic acid* ($C_2H_3[NH(C_7H_5O)]O_2$); *Benzoyl glycocoll* ($C_2H_4(C_7H_5O)NO_2$).—This acid is found in large quantities in the urine of herbivorous animals, but it also occurs in small quantities in the urine of man. It is derived partly from certain constituents of vegetable diet, and partly from the natural disintegration of tissue.

The relationship between hippuric acid and benzoic acid is to be noted. The urine of a cow or horse when at rest yields, by the action of hydrochloric acid, hippuric acid; but if the animals are being actively worked, their urine yields benzoic acid, and not hippuric acid.

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Moreover, the *fresh urine only* yields hippuric acid, the same urine when stale yielding benzoic acid. If benzoic acid be administered to an animal, hippuric acid is found in the urine.

The urine of children is said sometimes to contain benzoic acid.

Preparation.—(1.) Evaporate cows' urine to a thick syrup, and add to the concentrated urine an excess of hydrochloric acid. Hippuric acid will be deposited on standing.

(2.) By the action of benzoyl chloride on zinc glycocoll:—

$Zn''(C_2H_4NO_2)_2$	+	$2C_7H_5OCl$	=	$ZnCl_2$	+	$2C_9H_9NO_3$.
Zinc glycocoll	+	Benzoyl chloride	=	Zincic chloride	+	Hippuric acid.

Properties.—Rhombic prisms soluble in hot alcohol and in cold water (1 in 400). Solution acid. Forms crystallizable salts. The acid is monobasic. When heated it yields benzoic acid, benzoate of ammonia and benzonitrile, a coaly residue remaining in the vessel. It is converted into benzoic acid by sulphuric acid, and into benzoic acid and glycocine ($C_2H_5NO_2$) by hydrochloric acid. Nitrous acid converts it into benzoglycollic acid ($C_9H_8O_4$) which by the action of boiling water is converted into benzoic ($C_7H_6O_2$) and glycollic acids ($C_2H_4O_3$).

It is to be remarked that hippuric acid is soluble in an aqueous solution of sodic phosphate, which probably explains the acid reaction of the urine.

5. Salts.—These consist essentially of sulphuric, phosphoric, and hydrochloric acids, combined with soda and potash, and with lime and magnesia. The ash also contains a trace of iron.

The quantity of saline matter in normal urine varies between 8 and 9 grains in 1000 of urine, but the quantity is largely influenced by diet (an animal diet increasing the quantity of sulphates), by mental energy, etc.

6. Extractive Matter.—This includes kreatin, kreatinin (derived from the metamorphosis of muscular tissue), xanthin, and other bodies, such as indican, glucose, etc.

7. Pigments.—The pigments of the urine are not well understood. They are probably altered hæmoglobin. A body called *urohæmatin* has been mentioned by Harley, and one called *urochrome* by Thudichum. Other pigments variously named purpurin, rosacic acid, and uroerythrin have also been described.

Schunck considers that all urinary pigments are products of two coloring matters always present, the one being soluble in ether, having the composition $C_{43}H_{51}NO_{26}$, and the other insoluble in ether, having the composition $C_{19}H_{27}NO_{14}$.

In jaundice the urine is colored by bile pigment.

8. Free Gases.—It was found that 100 c.c. of urine yielded at normal temperature and pressure the following gases:—

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Nitrogen	0·87
Oxygen	0·06
Carbonic anhydride, *free*	4·54
,, ,, *combined*	2·07

It is to be noted that the composition of the urine is largely influenced by disease. Thus albumen appears in Bright's disease, and glucose in diabetes.

Urinary Calculi.

A few general analytical remarks are all that is necessary here.

On heating a very small piece of the calculus on platinum foil, one of two results may occur :—

A. *It may be entirely, or very nearly entirely, dissipated.*

If this occurs, it is probably uric acid, but it may be urate of ammonia, cystine, or xanthin.

Calculus.	Physical Characters.	Action of Water, Alkalies, etc.	Action of Acids, etc.
Uric acid, $C_5N_4H_4O_3$.	Brownish red; smooth or tuberculated; concentric laminæ (common).	Insol. in water; sol. by heat in solution of KHO, without the generation of ammonia. A ppt. of uric acid occurs when an acid is added to the alkaline solution.	Dissolves with effervescence in HNO_3. The residue on evaporation is *red*, becoming purple red on the addition of ammonia (purple red murexide).
Urate of ammonia.	Clay colored; smooth; fine concentric laminæ (rare).	Sol. in water; sol. by heat in solution of KHO, ammonia fumes being evolved.	
Cystine ($C_3H_7NSO_2$).	Brownish yellow; semi-transparent; crystalline (very rare).	Insol. in water, in alcohol, or in ether; sol. in ammonia, when the solution is evaporated spontaneously, it leaves hexagonal plates. The ammonia solution is precipitated by an acid.	Odor of CS_2 when heated. Sol. in a solution of KHO. If acetate of lead be added to a boiling solution, a black ppt. of PbS results.
Xanthin ($C_5H_4N_4O_2$).	Pale brown; polished appearance (very rare).	Sol. in alkaline solutions.	Sol. in HNO_3 *without* effervescence; residue on evaporation a *deep yellow* color. Sol. in boiling HCl.

B. *It may not be dissipated by heat.*

It is probably oxalate of lime or fusible calculus, but it may be phosphate of lime or ammonio-phosphate of magnesia.

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Calculus.	Physical Characters.	Action of Ammonia on Solutions.	Action of Acids, Blow pipe, etc.
Oxalate of lime (mulberry calculus).	Deep brown; rough; very hard; layers thick (common).	The solution in HCl gives a white amorphous ppt. with ammonia.	Sol. in HCl without effervescence; insol. in acetic acid. When heated it becomes $CaCO_3$, when it dissolves in HCl with effervescence, but on being heated more strongly CaO only remains, which is alkaline to turmeric.
Phosphate of lime (bone earth calculus).	Pale brown color; laminæ regular (rare).	The solution in HCl gives a white amorphous gelatinous ppt. with ammonia.	Sol. in HCl; insol. in acetic acid. Infusible before the blow pipe. The residue on being strongly heated is not alkaline.
Ammonio-phosphate of magnesia (triple phosphate).	White, brittle, and crystalline; surface uneven; seldom laminated (rare).	The solution in acids gives a white crystalline ppt. with ammonia.	Sol. in HCl and in acetic acid. Fusible before blow-pipe with difficulty, evolving NH_3. Residue insol. in water and not alkaline.
Mixed phosphate of lime and ammonio-phosphate of magnesia (fusible calculus).	White; often very large; fusible and rarely laminated (common).	The solution in HCl or acetic acid gives a white ppt. with ammonia (phosphate of magnesia) and a white ppt. with oxalate of ammonia (lime).	Sol. in acetic acid; insol. in KHO. Very fusible by blow pipe, residue being insol. in water, but sol. in acids. Residue not alkaline.

Fæces.

These constitute the excrementitious portions of food. The chemical composition of the solid matter of the excrement varies with the food taken. The fæces consist (on an average) of about 25 per cent. of solid matter and the rest water. The solid portion is made up of biliary matter, alimentary débris, and salts, these latter being mainly phosphates of lime and magnesia, with small quantities of iron, soda, lime, and silica. The offensive odor of fæcal matter is due to certain intermediate products of oxidation, and becomes more offensive as the quantity of bile secreted diminishes.

Excretin ($C_{78}H_{156}SO_2$), a body melting at 204·8° F. (96° C.), soluble in water and hot alcohol, and insoluble in cold alcohol, has been discovered by Marcet in the alcoholic extract of fæcal matter.

Excretolic acid (Marcet) consists of a mixture of fatty acids, precipitated by the action of lime on the alcoholic extract of fæcal matter.

Sweat is the watery excretion from the sudoriparous glands of the skin. Its reaction is usually acid, from the presence of free lactic and formic acids, etc. It contains from 0·5 to 2·00 per cent. of solid

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matter, the quantity varying with the temperature of the day, the liquids taken, the amount of exercise, etc. The chief part of the solid matter consists of sodic chloride, but traces of phosphate of lime, and of lactates, butyrates, and acetates are also present. A trace of urea is said to be constant. A peculiar azotized and easily decomposed body and an odorous principle are present in varying quantity. Carbonic acid and nitrogen are also given off by the skin.

Mucus is a viscid matter secreted by the mucous membranes. It is always, more or less largely, mixed with epithelium cells. Its glairy consistence is due to the presence of a nitrogenized body called *mucin*, the per-centage composition of which is said to be carbon 52·2, hydrogen 7·0, nitrogen 12·6, and oxygen 28·2.

Mucin swells up, but is not soluble in water. It is turned yellow by nitric acid. It is neither precipitated by mercuric chloride, nor by acetic acid, plumbic acetate, or potassic ferrocyanide, but is coagulated by alcohol and by heat.

Pus is a creamy-white fluid, having a neutral or slightly alkaline reaction. It appears under the microscope to consist of minute globules floating in a transparent serum. The pus globules are only imperfectly dissolved by alkalies. They contain fat (2 to 6 per cent.) and cholesterin (1 per cent.). Dilute acids distend them. The serum contains albumin, leucin, and the albuminoid body called "pyin."

Pyin is soluble in water. It is precipitated by acetic acid. Unlike mucin it is precipitated both by mercuric chloride and by lead acetate.

Cholesterin $C_{26}H_{43}OH$ is a fat-like body, soluble in ether, in boiling alcohol, and in chloroform. It is the chief constituent of biliary calculi.

The solid residue of pus contains 12 per cent. of saline matter, phosphoric acid and potash being the principal acid and base present.

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APPENDIX.

Liquefaction of Oxygen, Etc.—Since the chapter on oxygen was printed, M. Raoul Pictet of Geneva has effected the liquefaction of oxygen under a pressure of 300 atmospheres, and at the temperature produced by the evaporation of liquid carbonic dioxide in a vacuum. On removing the pressure a jet of liquid oxygen escaped from the tube. By a double circulation of SO_2 and CO_2, the liquefaction of the CO_2 was effected at a temperature of —85° F. (—65° C.) and at a pressure of 4 to 6 atmospheres. This liquid carbonic anhydride was then passed along a tube about 4 meters long, communicating with two air-pumps. By forming a vacuum with the pumps the CO_2 solidifies. Through the interior of this tube a second and smaller tube passes, through which a current of oxygen set free in a strong vessel can be passed.

The apparatus will stand a pressure of 800 atmospheres.—"Chemical News," Vol. xxxvi., p. 281.)

M. Pictet has also lately made the experiment of liquefying and solidifying hydrogen. The process consisted in the decomposition of potassic formate by potassic hydrate, by which means pure hydrogen is generated. Thirty-five minutes after the commencement of the experiment, a pressure of 650 atmospheres was reached, at which point it remained for some minutes. The tap of the apparatus being now opened, a bluish jet escaped with a crackling sound, like that produced by the contact of water and red-hot iron. The jet then suddenly ceased; and it appeared as if a hail of solid bodies was thrown violently with a rattling noise on the ground. The tap having been again closed, the pressure fell from 370 atmospheres to 320, at which it stood for a few minutes, then rising to 325. When the tap was once more turned, a jet again escaped, which underwent interruptions, showing that beyond doubt crystallisation had taken place in the interior of the tube. This was proved by the escape of the fluid hydrogen when the temperature was raised.

Mendeleeff's Law of Periodicity. — According to Mendeleeff ("Journal de la Soc. Chimique Russe," Tome i., p. 60), "*The*

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properties of simple bodies, the constitution of their combinations, as well as the properties of the latter, are periodic functions of the atomic weights of the elements."

In accordance with this law the elements are arranged in the order of their atomic weight as follows :—

Series.	1st Group.	2nd Group.	3rd Group.	4th Group.	5th Group.	6th Group.	7th Group.	8th Group.
	..	..	..	RH_4	RH_3	RH_2	RH	(R_2H)
	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	(RO_4)
1	H=1	..	..	..	..	..	..	..
2	Li=7	Be=9	B=11	C=12	N=14	O=16	F=19	..
								Cu=63
3	Na=23	Mg=24	Al=27	Si=28	P=31	S=32	Cl=35	Fe=56
4	K=39	Ca=40	? E=44	Ti=48	V=51	Cr=52	Mn=55	Co=59
								Ni=59
								Ru=104
5	(Cu=63)	Zn=65	? 68	? 72	As=75	Se=78	Br=80	Rh=104
6	Rb=85	Sr=87	Yt=88	Tr=90	Nb=94	Mo=96	? 100	Pd=106
								Ag=108
								Os=195
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Fe=125	I=127	Ir=197
8	Cs=133	Ba=137	Di=138 (?)	Ce=140	..	..	..	Pb=198
								Au=199
9	..	..	..	..	..	..	..	..
10	..	..	Er=178	La=180 ?	Ta=182	W=184	? 190	..
11	(199=Au)	200 Hg	Tl=204	Pb=207	Bi=208	..	..	..
12	..	..	..	Th=231	..	U=250	..	..

The chief use of this law at present appears to be in predicting the discovery of new metals and the properties of their compounds. It will be noticed that several gaps occur in this classification, which gaps Mendeleeff considers will be filled either by new metals or by the corrected atomic weights of known elements. The newly discovered metal, Gallium (*see* page 434), is, according to Mendeleeff, his eka-aluminium, El, Group 3, Series 5, At. Wt. = 68. (Real At. Wt. 69·9).

For further information on this subject see—

Mendeleeff's Foundations of Chemistry.

Liebig's Annalen, Supplement, Band viii., page 133 (1871).

"Chemical News." December 24th, 1875.

"Quarterly Journal of Science," No. xlix., January, 1876. Page 32 et seq.

In order that certain elements may fit into those places which

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Mendeleeff assigns to them, he proposes the following changes in the atomic weights of certain elements.

Element.	Numbers received.		Numbers proposed.		Remarks.
	At. Wt.	Oxide.	At. Wt.	Oxide.	
Indium ..	75	InO	113	In_2O_3	Specific heat as determined by Bunsen and by the author confirms this change.
Uranium ..	120	U_2O_3	240	UO_3	MM. Ramelsburg and Roscoe accept the proposed change.
Cerium ..	92	CeO Ce_3O_4	138	Ce_2O_3 CeO_2	The specific heat of cerium seems confirmatory.
Thorinum ..	116	ThO	232	ThO_2	MM. Chydemius and Delafontaine previously proposed the same change.
Yttrium ..	60	YO	90	Y_2O_3	M. Cleve accepts these formulæ.
Erbium ..	141	ErO	171	Er_2O_3	
Di ? or La ?	92	RO	138	R_2O_3	

From the *Chemical News*, December 24, 1875.

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Table I.

Table showing the Specific Gravities and percentage strengths of various solutions of Nitric Anhydride (N_2O_5) *and Nitric Acid* (HNO_3).

Specific Gravity.	HNO_3=63.	N_2O_5=108.	Specific Gravity.	HNO_3=63.	N_2O_5=108.
1·5000	92·983	79·700	1·2947	46·299	39·685
1·4980	92·053	78·903	1·2887	45·562	39·053
1·4960	91·124	78·106	1·2826	44·632	38·256
1·4940	90·194	77·309	1·2765	43·702	37·459
1·4910	89·264	76·512	1·2705	42·772	36·662
1·4880	88·334	75·715	1·2644	41·842	35·865
1·4850	87·404	74·918	1·2583	40·913	35·068
1·4820	86·484	74·121	1·2523	39·983	34·271
1·4790	85·545	73·324	1·2462	39·053	33·474
1·4760	84·615	72·527	1·2402	38·123	32·677
1·4730	83·680	71·730	1·2341	37·190	31·880
1·4700	82·755	70·933	1·2277	36·263	31·083
1·4670	81·825	70·136	1·2212	35·334	30·286
1·4640	80·895	69·339	1·2148	34·404	30·489
1·4600	79·966	68·542	1·2084	33·474	28·692
1·4570	79·036	67·745	1·2019	32·544	27·895
1·4530	78·106	66·948	1·1958	31·614	27·098
1·4500	77·181	66·155	1·1895	30·684	26·301
1·4460	76·246	65·354	1·1833	29·755	25·504
1·4424	75·316	64·557	1·1770	28·825	24·707
1·4385	74·386	63·760	1·1709	27·890	23·910
1·4346	73·457	62·963	1·1648	26·965	23·113
1·4306	72·527	62·166	1·1587	26·035	22·316
1·4269	71·587	61·369	1·1526	25·105	21·519
1·4228	70·667	60·572	1·1465	24·176	20·722
1·42 B. P.	70·000	60·000	1·1403	23·246	19·925
1·4189	69·737	59·775	1·1345	22·316	19·128
1·4147	68·807	58·978	1·1286	21·386	18·331
1·4107	67·878	58·181	1·1227	20·456	17·534
1·4065	66·948	57·384	1·1168	19·526	16·737
1·4023	66·018	56·587	1·1109	18·597	15·940
1·3978	65·090	55·790	1·1051	17·667	15·143
1·3945	64·158	54·993	1·1010	17·442	14·950
1·3882	63·229	54·196	1·0993	16·737	14·346
1·3833	62·299	53·399	1·0935	15·807	13·549
1·3783	61·369	52·602	1·0878	14·877	12·752
1·3732	60·439	51·805	1·0821	13·947	11·955
1·3681	59·579	51·068	1·0764	13·017	11·158
1·3630	58·579	50·211	1·0708	12·088	10·361
1·3579	57·650	49·414	1·0651	11·158	9·564
1·3529	56·720	48·617	1·0595	10·228	8·767
1·3477	55·790	47·820	1·0540	9·298	7·970
1·3427	54·860	47·023	1·0485	8·368	7·173
1·3376	53·930	46·226	1·0430	7·439	6·376
1·3323	53·000	45·429	1·0375	6·508	5·579
1·3270	52·069	44·632	1·0320	5·579	4·782
1·3216	51·141	43·835	1·0267	4·649	3·985
1·3163	50·211	43·038	1·0212	3·719	3·188
1·3110	49·281	42·241	1·0159	2·789	2·391
1·3056	48·355	41·447	1·0106	1·860	1·594
1·3001	47·180	40·440	1·0053	0·930	0·797

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TABLE II.

Showing the Percentage of real Sulphuric Acid (H_2SO_4) *corresponding to various Specific Gravities of Aqueous Sulphuric Acid.*

Bineau; Otto. Temp 15°.

Specific Gravity.	Per cent. of H_2SO_4.	Specific Gravity.	Per cent. of H_2SO_4.	Specific Gravity.	Per cent. of H_2SO_4.	Specific Gravity.	Per cent. of H_2SO_4.
1·8426	100	1·675	75	1·398	50	1·182	25
1·842	99	1·663	74	1·3886	49	1·174	24
1·8406	98	1·651	73	1·379	48	1·167	23
1·840	97	1·639	72	1·370	47	1·159	22
1·8384	96	1·627	71	1·361	46	1·1516	21
1·8376	95	1·615	70	1·351	45	1·144	20
1·8356	94	1·604	69	1·342	44	1·136	19
1·834	93	1·592	68	1·333	43	1·129	18
1·831	92	1·580	67	1·324	42	1·121	17
1·827	91	1·568	66	1·315	41	1·1136	16
1·822	90	1·557	65	1·306	40	1·106	15
1·816	89	1·545	64	1·2976	39	1·098	14
1·809	88	1·534	63	1·289	38	1·091	13
1·802	87	1·523	62	1·281	37	1·083	12
1·794	86	1·512	61	1·272	36	1·0756	11
1·786	85	1·501	60	1·264	35	1·068	10
1·777	84	1·490	59	1·256	34	1·061	9
1·767	83	1·480	58	1·2476	33	1·0536	8
1·756	82	1·469	57	1·239	32	1·0464	7
1·745	81	1·4586	56	1·231	31	1·039	6
1·734	80	1·448	55	1·223	30	1·032	5
1·722	79	1·438	54	1·215	29	1·0256	4
1·710	78	1·428	53	1·2066	28	1·019	3
1·698	77	1·418	52	1·198	27	1·013	2
1·686	76	1·408	51	1·190	26	1·0064	1

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Table III.

Table showing the percentage quantities of Hydrochloric Acid, Sp. Gr. 1·2, and of Hydrochloric Acid Gas contained in aqueous solutions of different Specific Gravities.

Specific Gravity.	Acid of Sp. Gr. 1·2.	Hydrochloric Acid Gas.	Specific Gravity.	Acid of Sp. Gr. 1·2.	Hydrochloric Acid Gas.
1·2000	100	40·777	1·0980	49	19·980
1·1982	99	40·369	1·0960	48	19·572
1·1964	98	39·961	1·0939	47	19·165
1·1946	97	39·554	1·0919	46	18·757
1·1928	96	39·146	1·0899	45	18·349
1·1910	95	38·738	1·0879	44	17·941
1·1893	94	38·330	1·0859	43	17·534
1·1875	93	37·923	1·0838	42	17·126
1·1857	92	37·516	1·0818	41	16·718
1·1846	91	37·108	1·0798	40	16·310
1·1822	90	36·700	1·0778	39	15·902
1·1802	89	36·292	1·0758	38	15·494
1·1782	88	35·884	1·0738	37	15·087
1·1762	87	35·476	1·0718	36	14·679
1·1741	86	35·068	1·0697	35	14·271
1·1721	85	34·660	1·0677	34	13·863
1·1701	84	34·252	1·0657	33	13·094
1·1681	83	33·845	1·0637	32	12·597
1·1661	82	33·437	1·0617	31	12·300
1·1641	81	33·029	1·0597	30	11·903
1·1620	80	32·621	1·0577	29	11·506
1·1599	79	32·213	1·0557	28	11·109
1·1578 B. P.	78	31·805	1·0537	27	10·712
1·1557	77	31·398	1·0517	26	10·316
1·1536	76	30·990	1·052	B. P.	10·290
1·1515	75	30·582	1·0497	25	0·919
1·1494	74	30·174	1·0477	24	9·922
1·1473	73	29·767	1·0457	23	9·126
1·1452	72	29·359	1·0437	22	8·729
1·1431	71	28·951	1·0417	21	8·332
1·1410	70	28·544	1·0397	20	7·935
1·1389	69	28·136	1·0377	19	7·538
1·1369	68	27·728	1·0357	18	7·141
1·1349	67	27·321	1·0337	17	6·745
1·1328	66	26·913	1·0318	16	6·348
1·1308	65	26·508	1·0388	15	5·951
1·1287	64	26·098	1·0279	14	5·554
1·1267	63	25·690	1·0259	13	5·158
1·1247	62	25·282	2·0239	12	4·762
1·1226	61	24·874	1·0220	11	4·365
1·1206	60	24·466	1·0200	10	3·998
1·1185	59	24·058	1·0180	9	3·571
1·1164	58	23·650	1·0160	8	3·174
1·1143	57	23·242	1·0140	7	2·778
1·1123	56	22·834	1·0120	6	2·381
1·1102	55	22·426	1·0110	5	1·984
1·1082	54	22·019	1·0080	4	1·588
1·1061	53	21·611	1·0060	3	1·191
1·1041	52	21·203	1·0040	2	0·795
1·1020	51	20·796	1·0020	1	0·397
1·1000	50	20·388			

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TABLE IV.

Showing the Percentage Amount of Ammonia (NH_3) *in Aqueous Solutions of the Gas of various Specific Gravities.*

Carius. Temp. 14°.

Specific Gravity.	NH_3 per cent.	Specific Gravity.	NH_3 per cent.	Specific Gravity.	NH_3 per cent.
0·8844	36	0·9133	24	0·9520	12
0·8864	35	0·9162	23	0·9556	11
0·8885	34	0·9191	22	0·9593	10
0·8907	33	0·9221	21	0·9631	9
0·8929	32	0·9251	20	0·9670	8
0·8953	31	0·9283	19	0·9709	7
0·8976	30	0·9314	18	0·9749	6
0·9001	29	0·9347	17	0·9790	5
0·9026	28	0·9380	16	0·9831	4
0·9052	27	0·9414	15	0·9873	3
0·9078	26	0·9449	14	0·9915	2
0·9106	25	0·9484	13	0·9959	1

TABLE V.

Showing the Percentage Amount of Potash (K_2O) *in Aqueous Solutions of various Specific Gravities.*

Tünnermann, N. Tr. xviii., 2, 5. Temp. 15°.

Specific Gravity.	Per Cent. of K_2O.	Specific Gravity.	Per Cent. of K_2O.
1·3300	28·290	1·1437	14·145
1·3131	27·158	1·1308	13·013
1·2966	26·027	1·1182	11·882
1·2805	24·895	1·1059	10·750
1·2648	23·764	1·0938	9·619
1·2493	22·632	1·0819	8·487
1·2342	21·500	1·0703	7·355
1·2268	20·935	1·0589	6·224
1·2122	19·803	1·0478	5·002
1·1979	18·671	1·0369	3·961
1·1839	17·540	1·0260	2·829
1·1702	16·408	1·0153	1·697
1·1568	15·277	1·0050	0·5658

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TABLE VI.

Showing Percentage Amount of Soda (Na_2O) *in Aqueous Solutions of various Specific Gravities.*

Tünnermann.

Specific Gravity.	Per cent. of Na_2O.	Specific Gravity.	Per cent. of Na_2O.	Specific Gravity.	Per cent. of Na_2O.	Specific Gravity.	Per cent. of Na_2O.
1·4285	30·220	1·3198	22·363	1·2392	15·110	1·1042	7·253
1·4193	29·616	1·3143	21·894	1·2280	14·500	1·0948	6·648
1·4101	29·011	1·3125	21·758	1·2178	13·901	1·0855	6·044
1·4011	28·407	1·3053	21·154	1·2058	13·297	1·0764	5·440
1·3923	27·802	1·2982	20·550	1·1948	12·692	1·0675	4·835
1·3836	27·200	1·2912	19·945	1·1841	12·088	1·0587	4·231
1·3751	26·594	1·2843	19·341	1·1734	11·484	1·0500	3·626
1·3668	25·989	1·2775	18·730	1·1630	10·879	1·0414	3·022
1·3586	25·385	1·2708	18·132	1·1528	10·275	1·0330	2·418
1·3505	24·780	1·2642	17·528	1·1428	9·670	1·0246	1·813
1·3426	24·176	1·2578	16·923	1·1330	9·066	1·0163	1·209
1·3349	23·572	1·2515	16·379	1·1233	8·462	1·0081	0·604
1·3273	22·967	1·2453	15·714	1·1137	7·857	1·0040	0·302

TABLE VII.

Proportion of Absolute Alcohol by Weight in 100 *parts of Spirit, of different Specific Gravities at* 60° F.

(Fownes. *Phil. Trans.*, 1847.)

Alcohol per cent.	Specific Gravity.	Alcohol per cent.	Specific Gravity.	Alcohol per cent.	Specific Gravity.	Alcohol per cent.	Specific Gravity.
0·5	1·0000	25	·9652	51	·9160	76	·8581
0	0·9991	26	·9638	52	·9135	77	·8557
1	0·9981	27	·9623	53	·9113	78	·8533
2	0·9965	28	·9609	54	·9090	79	·8508
3	0·9947	29	·9593	55	·9069	80	·8483
4	0·9930	30	·9578	56	·9047	81	·8459
5	0·9914	31	·9560	57	·9025	82	·8434
6	0·9898	32	·9544	58	·9001	83	·8408
7	0·9884	33	·9528	59	·8979	84	·8382
8	0·9869	34	·9511	60	·8956	85	·8357
9	0·9855	35	·9490	61	·8932	86	·8331
10	0·9841	36	·9470	62	·8908	87	·8305
11	0·9828	37	·9452	63	·8886	88	·8279
12	0·9815	38	·9434	64	·8863	89	·8254
13	0·9802	39	·9416	65	·8840	90	·8228
14	0·9789	40	·9396	66	·8816	91	·8199
15	0·9778	41	·9376	67	·8793	92	·8172
16	0·9766	42	·9356	68	·8769	93	·8145
17	0·9753	43	·9335	69	·8745	94	·8118
18	0·9741	44	·9314	70	·8721	95	·8089
19	0·9728	45	·9292	71	·8696	96	·8061
20	0·9716	46	·9270	72	·8672	97	·8031
21	0·9704	47	·9249	73	·8649	98	·8001
22	0·9691	48	·9228	74	·8625	99	·7969
23	0·9678	49	·9206	75	·8603	100	·7938
24	0·9665	50	·9184				

In this Table every alternate number is the result of a direct synthetical experiment; absolute alcohol and distilled water being weighed out in the proper proportions, and mixed by agitation in stoppered bottles; after a lapse of three or four days, each specimen was brought exactly to 60° F. and the specific gravity determined with great care.

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TABLE VIII.

Specific Gravities corresponding to Degrees of Baumé's Hydrometer for Liquids heavier than Water. (*Water*=1·000.)

Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.
0	1·000	20	1·152	40	1·357	60	1·652
1	1·007	21	1·160	41	1·369	61	1·670
2	1·013	22	1·169	42	1·382	62	1·689
3	1·020	23	1·178	43	1·395	63	1·708
4	1·027	24	1·188	44	1·407	64	1·727
5	1·034	25	1·197	45	1·420	65	1·747
6	1·041	26	1·206	46	1·434	66	1·767
7	1·048	27	1·216	47	1·448	67	1·788
8	1·056	28	1·225	48	1·462	68	1·809
9	1·063	29	1·235	49	1·476	69	1·831
10	1·070	30	1·245	50	1·490	70	1·854
11	1·078	31	1·256	51	1·495	71	1·877
12	1·085	32	1·267	52	1·520	72	1·900
13	1·094	33	1·277	53	1·535	73	1·924
14	1·101	34	1·288	54	1·551	74	1·949
15	1·109	35	1·299	55	1·567	75	1·974
16	1·118	36	1·310	56	1·583	76	2·000
17	1·126	37	1·321	57	1·600		
18	1·134	38	1·333	58	1·617		
19	1·143	39	1·345	59	1·634		

Specific Gravities on Baumé's Scale for Liquids lighter than Water.

Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.
10	1·000	23	0·918	36	0·849	49	0·789
11	0·993	24	0·913	37	0·844	50	0·785
12	0·986	25	0·907	38	0·839	51	0·781
13	0·980	26	0·901	39	0·834	52	0·777
14	0·973	27	0·896	40	0·830	53	0·773
15	0·967	28	0·890	41	0·825	54	0·768
16	0·960	29	0·885	42	0·820	55	0·764
17	0·954	30	0·880	43	0·816	56	0·760
18	0·948	31	0·874	44	0·811	57	0·757
19	0·942	32	0·869	45	0·807	58	0·753
20	0·936	33	0·864	46	0·802	59	0·749
21	0·930	34	0·859	47	0·798	60	0·745
22	0·924	35	0·854	48	0·794		

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Table IX.

Degrees on Twaddell's Hydrometer, and the corresponding Specific Gravities.

[Note.—The degrees of Twaddell's hydrometer are converted into their corresponding specific gravities by multiplying by 0·005, and adding 1·000.]

Degrees Twaddell.	Specific Gravity.	Degrees Twaddell.	Specific Gravity.	Degrees Twaddell.	Specific Gravity.
1	1·005	8	1·040	15	1·075
2	1·010	9	1·045	16	1·080
3	1·015	10	1·050	17	1·085
4	1.020	11	1·055	18	1·090
5	1·025	12	1·060	19	1·095
6	1·030	13	1·065	20	1·100
7	1·035	14	1·070		

Table X.

English Weights and Measures.—Avoirdupois.

	Grs.	Drms.	Ozs.	lbs.	Qrs.	Cwt.	Tons.
Grain	1						
Drachm ..	27·34	1					
Ounce.. ..	437·5	16	1				
Pound.. ..	7000	256	16	1			
Quarter ..	196000	7168	448	28	1		
Cwt.	784000	28672	1792	112	4	1	
Ton	15680000	573440	35840	2240	80	20	1

Troy Weight.

	Grains.	Dwts.	Ounces.	lb.
Grain	1			
Pennyweight	24	1		
Ounce..	480	20	1	
Pound..	5760	240	12	1

1 cubic inch of distilled water in air at 62° F. = 252·456 grains.
1 cubic inch of distilled water *in vacuo* at 62° F. = 252·722 grains.

Cubic inches.

1 gallon = 277·276 (100 c.i. = 0·3606 gallon).
1 pint = 34·659
1 fluid ounce = 1·7329
1 litre = 61·024
1 cubic centimètre = 0·061024

1 cubic inch = 16·387 cubic centimètres.

(*For comparison of French and English weights, see page* 50.)

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TABLE XI.

To Reduce Grammes to Grains.

Log. Grammes + 1·188432 = log. Grains.

To Reduce Cubic Centimètres to Cubic Inches.

Log. cubic centimètres + (−2·7855007) = log. Cubic inches.

To Reduce Millimètres to Inches.

Log. millimétres + (−2·5951663) = log. inches.

To Convert Grains into Grammes.

Log. grains + (−2·8115680) = log. grammes.

To Convert Cubic Inches into Cubic Centimètres.

Log. cubic inches + 1·2144993 = log. cubic centimètres.

To Convert Inches into Millimètres.

Log. inches + 1·4048337 = log. millimètres.

TABLE XII.

Table of the corresponding Heights of the Barometer in Millimètres and English Inches.

Milli-mètres.	=	English inches.	Milli-mètres.	=	English inches.	Milli-mètres.	=	English inches.
720	=	28·347	739	=	29·095	758	=	29·843
721	=	28·386	740	=	29·134	759	=	29·882
722	=	28·425	741	=	29·174	760	=	29·922
723	=	28·465	742	=	29·213	761	=	29·961
724	=	28·504	743	=	29·252	762	=	30·000
725	=	28·543	744	=	29·292	763	=	30·039
726	=	28·583	745	=	29·331	764	=	30·079
727	=	28·622	746	=	29·370	765	=	30·118
728	=	28·662	747	=	29·410	766	=	30·158
729	=	28·701	748	=	29·449	767	=	30·197
730	=	28·740	749	=	29·488	768	=	30·236
731	=	28·780	750	=	29·528	769	=	30·276
732	=	28·819	751	=	29·567	770	=	30·315
733	=	28·858	752	=	29·606	771	=	30·355
734	=	28·898	753	=	29·645	772	=	30·394
735	=	28·937	754	=	29·685	773	=	30·433
736	=	28·976	755	=	29·724	774	=	30·473
737	=	29·016	756	=	29·764	775	=	30·512
738	=	29·055	757	=	29·803			

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Table XIII.

For Converting Degrees of the Centigrade Thermometer into Degrees of Fahrenheit's Scale.

Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.
−90°	−130°	−60°	−76°	−30°	−22°
85	121	55	67	25	13
80	112	50	58	20	4
75	103	45	49	15	+ 5
70	94	40	40	10	14
65	85	35	31	5	23
0°	+32°	+100°	+212°	+200°	+392°
+ 5	41	105	221	205	401
10	50	110	230	210	410
15	59	115	239	215	419
20	68	120	248	220	428
25	77	125	257	225	437
30	86	130	266	230	446
35	95	135	275	235	455
40	104	140	284	240	464
45	113	145	293	245	473
50	122	150	302	250	482
55	131	155	311	255	491
60	140	160	320	260	500
65	149	165	329	265	509
70	158	170	338	270	518
75	167	175	347	275	527
80	176	180	356	280	536
85	185	185	365	285	545
90	194	190	374	290	554
95	203	195	383	295	563

1° C.	=	1·8° F.
2	=	3·6
3	=	5·4
4	=	7·2

To Convert F. into C. degrees and C. into F. degrees.

$$\frac{(\text{F.}^\circ - 32) \times 5}{9} = \text{C.}^\circ\text{; or } (\text{F.}^\circ - 32) \div 1{\cdot}8 = \text{C.}^\circ$$

$$\frac{\text{C.}^\circ \times 9}{5} + 32 = \text{F.}^\circ\text{; or } (\text{C.}^\circ \times 1{\cdot}8) + 32 = \text{F.}^\circ$$

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TABLE XIV.

Table of the Tension of Aqueous Vapor expressed in Inches of Mercury, at 32° F., *for each degree* F. *between* 0° *and* 100°.

Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.
0	0·0439	26	0·1395	51	0·3742	76	0·8964
1	0·0459	27	0·1457	52	0·3882	77	0·9266
2	0·0481	28	0·1522	53	0·4026	78	0·9577
3	0·0503	29	0·1589	54	0·4175	79	0·9898
4	0·0526	30	0·1660	55	0·4329	80	1·0227
5	0·0551	31	0·1733	56	0·4488	81	1·0566
6	0·0576	32	0·1810	57	0·4653	82	1·0915
7	0·0603	33	0·1883	58	0·4822	83	1·1274
8	0·0630	34	0·1959	59	0·4997	84	1·1643
9	0·0659	35	0·2038	60	0·5178	85	1·2023
10	0·0689	36	0·2119	61	0·5364	86	1·2413
11	0·0721	37	0·2204	62	0·5556	87	1·2815
12	0·0753	38	0·2291	63	0·5755	88	1·3228
13	0·0788	39	0·2381	64	0·5959	89	1·3652
14	0·0823	40	0·2475	65	0·6170	90	1·4088
15	0·0861	41	0·2571	66	0·6388	91	1·4537
16	0·0899	42	0·2672	67	0·6612	92	1·4998
17	0·0940	43	0·2775	68	0·6843	93	1·5471
18	0·0982	44	0·2882	69	0·7081	94	1·5958
19	0·1027	45	0·2993	70	0·7327	95	1·6457
20	0·1073	46	0·3108	71	0·7580	96	1·6971
21	0·1121	47	0·3226	72	0·7841	97	1·7498
22	0·1171	48	0·3349	73	0·8109	98	1·8039
23	0·1223	49	0·3476	74	0·8386	99	1·8595
24	0·1278	50	0·3607	75	0·8671	100	1·9170
25	0·1335						

This Table is computed from Regnault's experiments, and is taken from Dixon's "Treatise on Heat" (page 257).

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