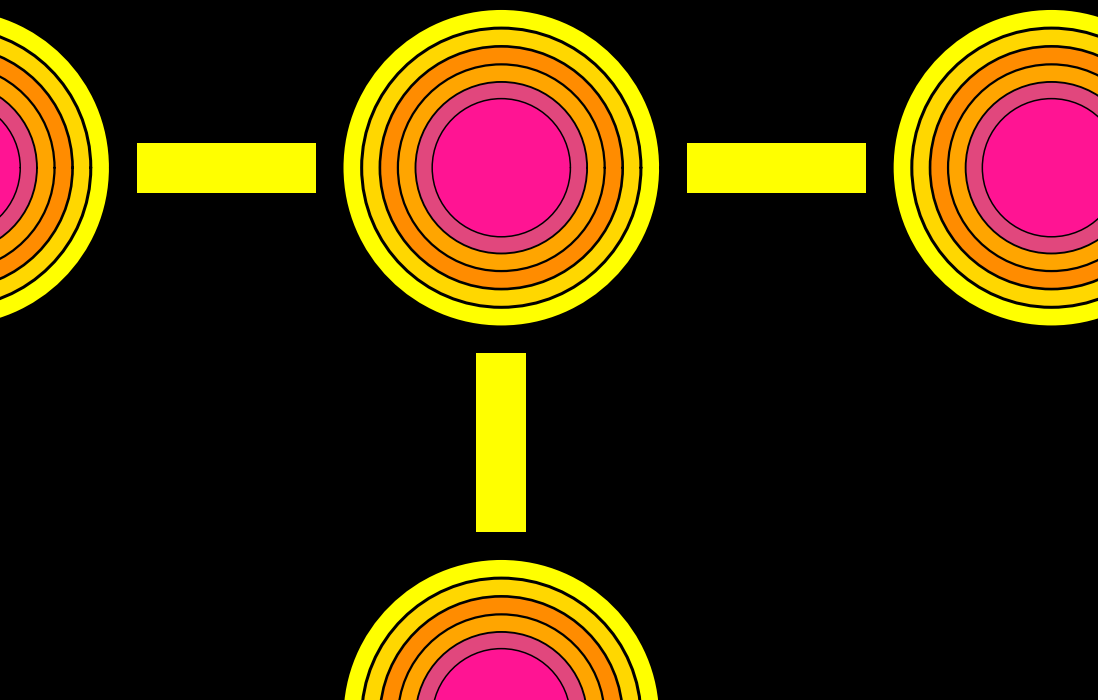


General Chemistry

N. L. Glinka

Volume

2



Nikolai Glinka, after graduating from the Moscow University in 1908, conducted research for several years under the guidance of N D Zelinsky. He preferred teaching to research, however, and took his doctorate in that field. He taught chemistry in Podolsk for twelve years, and was then transferred to Moscow in 1924 by the People's Commissariat of Education. In 1940, he was appointed Head of the Department of Inorganic and General Chemistry at the All-Union Polytechnical Correspondence Institute, a post he held to the end of his life. He died in 1965 at the age of 82

Veniamin Rabinovich, the editor of the revised edition of General Chemistry graduated from the Leningrad State University in 1940. He is a Candidate of Sciences (Chemistry) and an associate professor at the A. I. Gertsen Pedagogical Institute, Leningrad. He is the author of over 50 scientific works, mainly on the thermodynamics of electrolyte solutions. His other activities include the publication of reference literature: he is the deputy editor in chief and a coauthor of the fundamental seven-volume Chemist's Handbook (in Russian), and the editor and a coauthor of a Concise Chemical Reference Book (in Russian).

Mendeleev's Periodic Table of the Elements

Groups of elements →

Periods	Rows	I	II	III	IV	V	VI	VII	VIII		
1	I	(H)						1 H 1.0079 Hydrogen	2 He 4.00280 Helium	Atomic masses are given according to the International Table of 1977. The accuracy of the last significant digit is ±1 or ±3 if it is set in small type. The numbers in brackets are the mass numbers of the most stable isotopes. The names and symbols of elements in parentheses are not generally adopted.	
2	II	3 Li 6.941 Lithium	4 Be 9.01218 Beryllium	5 B 10.81 Boron	6 C 12.011 Carbon	7 N 14.0067 Nitrogen	8 O 15.9994 Oxygen	9 F 18.998403 Fluorine	10 Ne 20.179 Neon		
3	III	11 Na 22.98977 Sodium	12 Mg 24.305 Magnesium	13 Al 26.98154 Aluminium	14 Si 28.0855 Silicon	15 P 30.97376 Phosphorus	16 S 32.06 Sulphur	17 Cl 35.453 Chlorine	18 Ar 39.948 Argon		
4	IV	19 K 39.0983 Potassium	20 Ca 40.08 Calcium	21 Sc 44.9559 Scandium	22 Ti 47.90 Titanium	23 V 50.9415 Vanadium	24 Cr 51.996 Chromium	25 Mn 54.9380 Manganese	26 Fe 55.847 Iron	27 Co 58.9332 Cobalt	28 Ni 58.70 Nickel
	V	29 Cu 63.546 Copper	30 Zn 65.38 Zinc	31 Ga 69.72 Gallium	32 Ge 72.59 Germanium	33 As 74.9216 Arsenic	34 Se 78.96 Selenium	35 Br 79.904 Bromine	36 Kr 83.80 Krypton		
5	VI	37 Rb 85.4678 Rubidium	38 Sr 87.62 Strontium	39 Y 88.9059 Yttrium	40 Zr 91.22 Zirconium	41 Nb 92.9064 Niobium	42 Mo 95.94 Molybdenum	43 Tc 98.9062 Technetium	44 Ru 101.07 Ruthenium	45 Rh 102.9055 Rhodium	46 Pd 106.4 Palladium
	VII	47 Ag 107.868 Silver	48 Cd 112.41 Cadmium	49 In 114.82 Indium	50 Sn 118.69 Tin	51 Sb 121.75 Antimony	52 Te 127.60 Tellurium	53 I 126.9045 Iodine	54 Xe 131.30 Xenon		
6	VIII	55 Cs 132.9054 Cesium	56 Ba 137.33 Barium	57 La★ 138.9055 Lanthanum	72 Hf 178.49 Hafnium	73 Ta 180.9479 Tantalum	74 W 183.85 Tungsten	75 Re 186.207 Rhenium	76 Os 190.2 Osmium	77 Ir 192.22 Iridium	78 Pt 195.09 Platinum
	IX	79 Au 196.9665 Gold	80 Hg 200.59 Mercury	81 Tl 204.37 Thallium	82 Pb 207.2 Lead	83 Bi 208.9804 Bismuth	84 Po 209 Polonium	85 At [210] Astatine	86 Rn [222] Radon		
7	X	87 Fr [223] Francium	88 Ra 226.0254 Radium	89 Ac★★ [227] Actinium	104 Ku [261] Kurchatovium	105 [262] [261] [261]					

s-elements

p-elements

d-elements

f-elements

Distribution of electrons by unfilled and following completed sublevels

U92
238.029
Uranium

Distribution of electrons by levels

Atomic mass Atomic number

U	92
238.029	2
Uranium	2

■ s-elements ■ p-elements
■ d-elements ■ f-elements

Distribution of electrons by unfilled and following completed sublevels

Distribution of electrons by levels

★ Lanthanides

Ce 58 140.12 Cerium	Pr 59 140.9077 Praseodymium	Nd 60 144.24 Neodymium	Pm 61 [145] Promethium	Sm 62 150.4 Samarium	Eu 63 151.965 Europium	Gd 64 157.25 Gadolinium	Tb 65 158.9254 Terbium	Dy 66 162.50 Dysprosium	Ho 67 164.9304 Holmium	Er 68 167.26 Erbium	Tm 69 168.9342 Thulium	Yb 70 173.04 Ytterbium	Lu 71 174.967 Lutetium

★★ Actinides

Th 90 232.0381 Thorium	Pa 91 231.0359 Protactinium	U 92 238.029 Uranium	Np 93 237.0482 Neptunium	Pu 94 [244] Plutonium	Am 95 [243] Americium	Cm 96 [247] Curium	Bk 97 [247] Berkelium	Cf 98 [251] Californium	Es 99 [254] Einsteinium	Fm 100 [257] Fermium	Md 101 [258] Mendelevium	(No) 102 [259] (Nobelium)	(Lr) 103 [260] (Lawrencium)



Н. Л. Глинка

Общая Химия

**Под редакцией канд. хим. наук
В. А. РАБИНОВИЧА**

**Издательство «Химия»
Ленинград**

General Chemistry

N. L. Glinka

Volume 2

Edited by V. Rabinovich

Translated from the Russian
by G. Leib

Mir Publishers
Moscow

First published, 1958
Second edition, 1970
Third edition, 1981
Revised from the 1980 enlarged and updated Russian edition
Second printing, 1986

На английском языке

© Издательство «Химия», 1980
© Mir Publishers, English translation, 1981

CONTENTS

Chapter 1. Hydrogen	9
1. Occurrence and Preparation	9
2. Properties and Uses	11
3. Hydrogen Peroxide H_2O_2	14
Chapter 2. The Halogens	18
4. Occurrence. Physical Properties	19
5. Chemical Properties	22
6. Preparation and Uses	25
7. Hydrogen Halides	27
8. Oxygen Compounds	33
Chapter 3. The Main Subgroup of Group Six	40
Oxygen	41
9. Oxygen in Nature. Air	41
10. Preparation and Properties of Oxygen	43
11. Ozone	45
Sulphur, Selenium, Tellurium	47
12. Occurrence and Preparation of Sulphur	47
13. Properties and Uses of Sulphur	48
14. Hydrogen Sulphide. Sulphides	50
15. Sulphur Dioxide. Sulphurous Acid	53
16. Sulphur Trioxide. Sulphuric Acid	54
17. Production and Uses of Sulphuric Acid	59
18. Persulphuric Acid	61
19. Thiosulphuric Acid	62
20. Halogen Compounds of Sulphur	63
21. Selenium. Tellurium	63
Chapter 4. The Main Subgroup of Group Five	66
Nitrogen	67
22. Occurrence of Nitrogen. Preparation and Properties	67
23. Ammonia and Its Salts	68
24. Fixation of Atmospheric Nitrogen. Preparation of Ammonia	73
25. Hydrazine. Hydroxylamine. Hydrazoic Acid	76

26. Oxides of Nitrogen	77
27. Nitrous Acid	82
28. Nitric Acid	82
29. The Industrial Production of Nitric Acid	85
30. Nitrogen Cycle in Nature	86
Phosphorus	87
31. Occurrence. Preparation and Properties	87
32. Phosphorus Compounds with Hydrogen and the Halogens	90
33. Oxides and Acids of Phosphorus	90
34. Mineral Fertilizers	93
Arsenic, Antimony, Bismuth	94
35. Arsenic	94
36. Antimony	98
37. Bismuth	99
Chapter 5. The Main Subgroup of Group Four	101
Carbon	
38. Occurrence	102
39. Allotropy of Carbon	103
40. Chemical Properties of Carbon. Carbides	107
41. Carbon Dioxide. Carbonic Acid	108
42. Carbon Monoxide	112
43. Compounds of Carbon with Sulphur and Nitrogen	115
44. Fuel and Its Kinds	116
45. Gaseous Fuel	118
Organic Compounds	120
46. General	120
47. Features of Organic Compounds	121
48. The Theory of the Chemical Structure of Organic Compounds	123
49. Classification of Organic Compounds	134
50. Saturated Hydrocarbons (Alkanes)	137
51. Unsaturated Hydrocarbons	141
52. Saturated Cyclic Hydrocarbons (Cycloalkanes)	144
53. Aromatic Hydrocarbons	144
54. Halogen Derivatives of Hydrocarbons	149
55. Alcohols and Phenols	150
56. Ethers	154
57. Aldehydes and Ketones	154
58. Carboxylic Acids	157
59. Carboxylic Acid Esters. Fats	159
60. Carbohydrates	161
61. Amines	166
62. Amino Acids and Proteins	168
63. Natural and Synthetic High-Molecular Compounds (Polymers)	169
Silicon	177
64. Occurrence. Preparation and Properties	177
65. Compounds of Silicon with Hydrogen and the Halogens	179
66. Silicon Dioxide	181
67. Silicic Acids and Their Salts	181
68. Glass	184
69. Ceramics	186
70. Cement	187
71. Organosilicon Compounds	188

Germanium, Tin, Lead	190
72. Germanium	190
73. Tin	191
74. Lead	194
75. The Lead Accumulator	197
Chapter 6. Common Properties of Metals. Alloys	199
76. Physical and Chemical Properties of Metals. The Electron Structure of Metals, Dielectrics, and Semiconductors	199
77. The Crystalline Structure of Metals	204
78. Extraction of Metals from Their Ores	207
79. Production of Highly Pure Metals	210
80. Alloys	211
81. Phase Diagrams of Metal Systems	212
82. Corrosion of Metals	223
Chapter 7. First Group of the Table	230
Alkali Metals	230
83. Occurrence. Preparation and Properties	231
84. Sodium	234
85. Potassium	237
Copper Subgroup	238
86. Copper	239
87. Silver	245
88. Gold	249
Chapter 8. Complex Compounds	251
89. Fundamentals of the Coordination Theory	252
90. Basic Types and Nomenclature of Complex Compounds	255
91. Spatial Structure and Isomerism	260
92. Nature of the Chemical Bond in Complex Compounds	263
93. Stability of Complex Compounds in Solutions	270
94. Influence of Coordination on the Properties of Ligands and the Central Atom. Mutual Influence of Ligands	274
Chapter 9. Second Group of the Periodic Table	277
Main Subgroup	277
95. Beryllium	279
96. Magnesium	282
97. Calcium	284
98. Hardness of Natural Water and Its Elimination	286
99. Strontium. Barium	288
Secondary Subgroup	289
100. Zinc	290
101. Cadmium	295
102. Mercury	295
Chapter 10. Third Group of the Periodic Table	299
Main Subgroup	299
103. Boron	300

104. Aluminium	304
105. Gallium. Indium. Thallium	309
Secondary Subgroup. Lanthanides. Actinides	310
106. Scandium Subgroup	310
107. Lanthanides	311
108. Actinides	314
Chapter 11. Secondary Subgroups of Groups IV, V, VI, and VII	317
109. General Characteristic of the Transition Elements	317
Titanium Subgroup	319
110. Titanium	320
111. Zirconium. Hafnium	321
Vanadium Subgroup	322
112. Vanadium	323
113. Niobium. Tantalum	324
Chromium Subgroup	325
114. Chromium	325
115. Molybdenum	330
116. Tungsten	332
Manganese Subgroup	333
117. Manganese	334
118. Rhenium	337
Chapter 12. Eighth Group of the Periodic Table	339
Noble Gases	339
119. General	339
120. Helium	341
121. Neon. Argon	342
Secondary Subgroup	342
Iron Family	343
122. Iron. Occurrence	343
123. Iron and Its Alloys in Engineering. The Development of Metallurgy in the USSR	344
124. Physical Properties of Iron. Phase Diagram of Iron-Carbon System	345
125. Production of Iron and Steel	351
126. Heat Treatment of Steel	356
127. Iron Alloys	359
128. Chemical Properties of Iron. Compounds of Iron	362
129. Cobalt	367
130. Nickel	368
Platinum Metals	371
131. General	371
132. Platinum	373
133. Palladium. Iridium	374
Name Index	376
Subject Index	378

1

HYDROGEN

Hydrogen (*Hydrogenium**) was discovered in the first half of the 16th century by the well-known physician and naturalist Philippus Paracelsus. In 1776, Henry Cavendish (England) established its properties and distinctions from other gases. Antoine Lavoisier was the first to obtain hydrogen from water, and he proved that water is a chemical compound of hydrogen and oxygen (1783).

Hydrogen has three isotopes: protium ^1H , deuterium ^2H or D, and tritium ^3H or T. Their mass numbers are 1, 2, and 3. Protium and deuterium are stable, tritium is radioactive with a half-life of 12.5 years. Natural compounds contain deuterium and protium on an average in the ratio 1 : 6800 (according to the number of atoms). Tritium is found in nature in negligibly small amounts.

The nucleus of the hydrogen atom ^1H contains one proton. The nuclei of deuterium and tritium include, in addition to a proton, one and two neutrons, respectively.

A hydrogen molecule consists of two atoms. Below are given selected properties characterizing the hydrogen atom and molecule:

Ionization energy of atom, eV	13.60
Affinity of atom to electron, eV	0.75
Relative electronegativity	2.1
Radius of atom, nm	0.046
Internuclear distance in molecule, nm	0.0741
Standard enthalpy of dissociation of molecules at 25 °C, kJ/mol	436.1

1. Occurrence and Preparation

Hydrogen is encountered on the Earth in the free state only in negligible amounts. It is sometimes evolved together with other gases during the eruptions of volcanoes, and also from oil wells in the

* Here and below, the Latin names of the elements will be indicated only when they differ from the English ones—*translator's note*.

extraction of oil. But compounds of hydrogen are very abundant. This is evident from its forming one-ninth of the mass of water. All vegetable and animal organisms, petroleum, hard, soft, and brown coal, natural gas, and a number of minerals contain hydrogen. The latter accounts for about one per cent of the entire mass of the Earth's crust, including water and air. When passing over to a percentage of the total number of atoms, however, the hydrogen content in the Earth's crust is 17%*.

Hydrogen is the most widespread element in cosmos. About half of the mass of the Sun and the majority of the stars fall to its share. It is contained in gaseous nebulae, in interstellar gas, and in stars. Inside the latter, hydrogen atom nuclei transform into helium atom nuclei. This process occurs with the evolution of energy. It is the main source of energy for many stars including the Sun. The rate of the process, i.e. the number of hydrogen nuclei transforming into helium nuclei in one cubic metre per second, is low. Hence, the amount of energy evolved in unit time per unit volume is also low. But owing to the enormous mass of the Sun, the total amount of energy generated and radiated by the Sun is very great. It corresponds to diminishing of the Sun's mass by about four million tonnes a second.

In industry, hydrogen is generally produced from natural gas. The latter, consisting mainly of methane, is mixed with water vapour (steam) and oxygen. When the mixture of gases is heated to 800 to 900 °C in the presence of a catalyst, a reaction occurs that can be depicted schematically by the equation:



The gas mixture obtained is separated. The hydrogen is purified and is either used at the place of production, or is transported to the place of use in steel cylinders under a high pressure.

Another important industrial method of producing hydrogen is its separation from coke-oven gas or from gases obtained in petroleum refining. It is performed by deep cooling, when all the gases except hydrogen liquefy.

* Such a great difference between the quantities expressing the hydrogen content as a percentage of the total number of atoms and in per cent by mass is explained by hydrogen atoms being much lighter than atoms of other elements, in particular of oxygen and silicon—the most widespread elements in the Earth's crust.

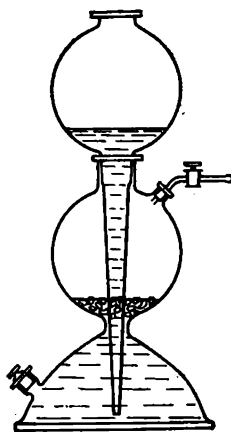


Fig. 1. Kipp gas generator

Hydrogen is customarily prepared in laboratories by the electrolysis of aqueous solutions of NaOH or KOH. The concentration of these solutions is selected such that corresponds to their maximum electrical conductivity (25% for NaOH and 34% for KOH). The electrodes are usually made from sheet nickel. This metal does not corrode in solutions of alkalis even when it is the anode. When necessary, the hydrogen obtained is purified of water vapour and of traces of oxygen. Among other laboratory methods, the greatest favour has been found by the method of liberating hydrogen from solutions of sulphuric or hydrochloric acids by acting on them with zinc. The reaction is usually conducted in a Kipp gas generator (Fig. 1).

2. Properties and Uses

Hydrogen is a colourless, odourless gas. At a temperature below -240°C (its critical temperature), it liquefies under pressure; the boiling point of liquid hydrogen is -252.8°C (at standard atmospheric pressure). If this liquid is rapidly evaporated, solid hydrogen is obtained in the form of transparent crystals melting at -259.2°C .

Hydrogen is the lightest of all gases; it is 14.5 times lighter than air. The mass of one litre of hydrogen in standard conditions is 0.09 g. Hydrogen dissolves in water very slightly, but in some metals such as nickel, palladium, and platinum, it dissolves quite considerably.

The ability of hydrogen to diffuse through metals is associated with its ability to dissolve in them. In addition, being the lightest gas, hydrogen has the highest rate of diffusion: its molecules diffuse in another substance and pass through various partitions and membranes faster than molecules of all other gases. Its diffusing power is especially great at high pressures and elevated temperatures. This is why work with hydrogen in such conditions is associated with considerable difficulties.

The diffusion of hydrogen in steel at elevated temperatures may cause the **hydrogen corrosion** of the steel. This absolutely unique kind of corrosion consists in the hydrogen reacting with the carbon in the steel and converting it into hydrocarbons (usually into methane). This sharply detracts from the properties of the steel.

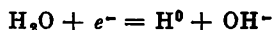
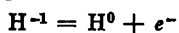
The chemical properties of hydrogen are determined to a considerable extent by the ability of its atoms to give up the only electron at their disposal and transform into positively charged ions. Here a feature of the hydrogen atom manifests itself that distinguishes it from the atoms of all the other elements: the absence of intermediate electrons between the valence electron and the nucleus. The hydrogen ion formed as a result of a hydrogen atom losing its electron is a proton whose size is less by several orders of magnitude than that of the cations of all other elements. Consequently, the polarizing action

of a proton is very great, owing to which hydrogen is not capable of forming ionic compounds in which it would play the role of a cation. Its compounds even with the most active non-metals, for instance with fluorine, are substances with a polar covalent bond.

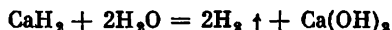
A hydrogen atom is capable of not only giving up, but also of attaching an electron. Here a negatively charged hydrogen ion having the electron shell of a helium atom is formed. In compounds with certain active metals, hydrogen is in the form of such ions. Hence, hydrogen displays a dual chemical nature—it has both an oxidizing and a reducing ability. In most reactions, it plays the role of a reducing agent and forms compounds in which its oxidation number is $+1$. But in reactions with active metals, it plays the role of an oxidizing agent: its oxidation number in compounds with metals is -1 .

Thus, when it gives up one electron, hydrogen is similar to the metals of Group I of the periodic table, and when it attaches an electron, it is similar to the non-metals of Group VII. This is the reason why hydrogen is usually placed either in the first group of the periodic table, and at the same time in the seventh group in parentheses, or vice versa.

Compounds of hydrogen with metals are called **hydrides**. The hydrides of the alkali and alkaline-earth metals are salts, i.e. the chemical bond between the metal and the hydrogen in them is ionic. They are white crystals, unstable and decomposing into the relevant metal and hydrogen when heated. The action of water on them causes an oxidation-reduction reaction to proceed in which the hydride ion H^- is the reducing agent, and the hydrogen of the water is the oxidizing one:



The products are hydrogen and a base. For example, calcium hydride reacts with water according to the equation:

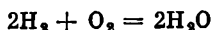


This reaction is used to determine the presence of traces of moisture and to remove them.

Metal-like and polymer hydrides are known in addition to the salt-like ones. Metal-like hydrides are close to metals as regards the nature of the chemical bond in them. They have a considerable electrical conductivity and a metallic lustre, but are very brittle. They include titanium, vanadium, and chromium hydrides. The metal atoms in polymer hydrides (for example, in zinc and aluminium hydrides) are bound to one another by means of hydrogen "bridges" as in boron hydrides (p. 302).

If we apply a lighted match to a stream of hydrogen emerging from a narrow orifice, the hydrogen ignites and burns with a non-luminous

flame forming water:



When a mixture of two volumes of hydrogen and one volume of oxygen is ignited, the gases combine virtually instantaneously throughout the entire mixture, and a strong explosion occurs. This is why the name **detonating gas** has been given to such a mixture. The standard enthalpy of this reaction per mole of liquid water formed is -285.8 kJ, and per mole of water vapour it is -241.8 kJ. Hence, a great amount of heat is evolved when hydrogen burns. The temperature of a hydrogen flame may reach 2800°C . A hydrogen-oxygen flame is used for welding and cutting metals, and for the melting of refractory metals.

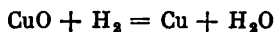
At low temperatures, hydrogen does not virtually react with oxygen. If the two gases are mixed and left standing, no traces of water will be found in the mixture even after several years have elapsed. But if a mixture of hydrogen and oxygen is placed in a vessel, the latter is soldered and kept at 300°C , some water will form in a few days. At 500°C , the hydrogen completely combines with the oxygen in a few hours, while when the mixture is heated to 700°C , the temperature rapidly rises, and the reaction terminates virtually instantaneously. Therefore, to make the mixture explode, it must be heated in at least one spot up to 700°C .

The low rate of reaction of hydrogen with oxygen at low temperatures is explained by the high activation energy of the reaction. Hydrogen and oxygen molecules are very stable. A collision between them at room temperature is not effective. Only at elevated temperatures, when the colliding molecules acquire a high kinetic energy, do some collisions of the molecules become effective and result in the formation of active centres.

Catalysts can greatly increase the rate of the hydrogen-oxygen reaction. If we introduce, for example, a small piece of platinized asbestos (i.e. asbestos coated with finely comminuted platinum) into a mixture of hydrogen and oxygen, the rate of the reaction will grow to such an extent that an explosion will occur in a short time.

We remind our readers that the reaction between hydrogen and oxygen is a chain one and proceeds according to a chain-branching mechanism (see Vol. 1, Sec. 62).

At elevated temperatures, hydrogen can take oxygen away from many compounds including most metal oxides. For instance, if hydrogen is passed over heated copper(II) oxide, the copper is reduced:

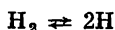


For this reason, hydrogen is employed in metallurgy to reduce certain non-ferrous metals from their oxides. Hydrogen finds its main application in the chemical industry for the synthesis of hydrogen

chloride (see Sec. 7), for the synthesis of ammonia (see Sec. 27), which is used, in turn, to produce nitric acid and nitrogen fertilizers, and for the preparation of methyl alcohol (see Sec. 55) and other organic compounds. It is used for the hydrogenation* of fats (p. 160), coal, and petroleum. In the hydrogenation of coal and petroleum, the low-grade kinds of fuel lean in hydrogen are converted into high-grade ones.

Hydrogen is used to cool powerful generators of electric current, while its isotopes are employed in atomic power engineering (see Vol. 1, pp. 118 and 224).

Atomic hydrogen. At elevated temperatures, hydrogen molecules dissociate into atoms:



This reaction can be achieved, for example, by heating a tungsten wire with current in an atmosphere of greatly rarefied hydrogen. The reaction is reversible, and equilibrium shifts to the right when the temperature rises. At 2000 °C, the degree of dissociation (i.e. the fraction of the molecules that dissociate) is only 0.1%, at 3000 °C it is 9%, at 4000 °C, 62.5%, and at 5000 °C it is 94.7% (all the figures are for a standard atmospheric pressure in the system).

Atomic hydrogen is also obtained when a silent electric discharge acts on molecular hydrogen under a pressure of about 70 Pa. The hydrogen atoms formed in these conditions do not immediately combine into molecules, which makes studying of their properties possible.

The decomposition of hydrogen into atoms is accompanied by the absorption of a great amount of heat:



Hence, it is evident that hydrogen atoms must be much more active than the molecules. For molecular hydrogen to enter into a reaction, the molecules must first decompose into atoms, for which a large amount of energy is needed. Reactions of atomic hydrogen do not need such an expenditure of energy.

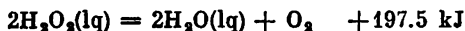
Indeed, atomic hydrogen already at room temperature reduces many metal oxides and directly combines with sulphur, nitrogen, and phosphorus; it forms hydrogen peroxide with oxygen.

3. Hydrogen Peroxide H_2O_2

Hydrogen peroxide is a colourless syrup-like liquid with a density of 1.45 g/cm³ that freezes at -0.48 °C. It is a very unstable substance that can decompose explosively into water and oxygen, a great

* Hydrogenation processes are based on the attachment of hydrogen to the molecules of the reactants.

amount of heat being evolved:



Aqueous solutions of hydrogen peroxide are more stable. They can be kept for a considerable time in a cool place. **Perhydrol**—a solution available on the market—contains 30% of H_2O_2 . This product and highly concentrated solutions of hydrogen peroxide contain stabilizing additions.

The decomposition of hydrogen peroxide is accelerated by catalysts. If, for example, we throw a small amount of manganese(IV) dioxide into a solution of hydrogen peroxide, a violent reaction occurs, and oxygen is liberated. The catalysts promoting the decomposition of hydrogen peroxide include copper, iron, manganese, and also the ions of these metals. Even traces of these metals can cause the decomposition of H_2O_2 .

Hydrogen peroxide is formed as an intermediate in the combustion of hydrogen, but owing to the high temperature of the hydrogen flame, it immediately decomposes into water and oxygen. If the hydrogen flame is directed onto a piece of ice, however, traces of hydrogen peroxide can be found in the water formed.

Hydrogen peroxide is also produced when atomic hydrogen reacts with oxygen.

Hydrogen peroxide is mainly produced on a commercial scale by electrochemical methods, for example by the anode oxidation of solutions of sulphuric acid or ammonium hydrogen sulphate with the subsequent hydrolysis of the persulphuric acid $\text{H}_2\text{S}_2\text{O}_8$ formed (see Sec. 18). The following processes occur:



In hydrogen peroxide, the hydrogen atoms are covalently bonded to the oxygen atoms between which there is also a single bond. The structure of hydrogen peroxide can be depicted by the formula $\text{H}-\text{O}-\text{O}-\text{H}$.

The H_2O_2 molecules have a considerable polarity ($\mu = 2.13 \text{ D}$), which is a result of their spatial structure (Fig. 2).

In a hydrogen peroxide molecule, the bonds between the hydrogen and oxygen atoms are polar (owing to shifting of the shared electrons towards the oxygen). Hence, in an aqueous solution under the influence of the polar

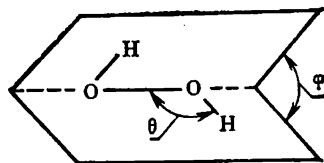


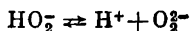
Fig. 2. Structure of an H_2O_2 molecule

The angle θ is close to 100° , the angle ϕ is close to 95° . The bond lengths are 0.097 nm ($\text{O}-\text{H}$) and 0.149 nm ($\text{O}-\text{O}$)

water molecules, hydrogen peroxide can detach hydrogen ions, i.e. it has acid properties. Hydrogen peroxide is a very weak dibasic acid ($K_1 = 2.6 \times 10^{-12}$); in an aqueous solution it decomposes, although insignificantly, into ions:

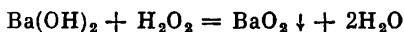


Dissociation in the second stage,

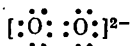


does not virtually occur. It is suppressed by the presence of water—a substance that dissociates with the formation of hydrogen ions to a greater extent than hydrogen peroxide. If the hydrogen ions are bound, however (for example, when an alkali is introduced into the solution), dissociation in the second stage does occur.

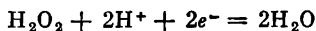
Hydrogen peroxide reacts directly with some bases and forms salts. For instance, when hydrogen peroxide is added to an aqueous solution of barium hydroxide, the barium salt of hydrogen peroxide precipitates:



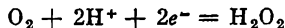
Salts of hydrogen peroxide are called **peroxides**. They consist of positively charged metal ions and negatively charged O_2^{2-} ions whose electron dot formula is as follows:



The oxidation number of oxygen in hydrogen peroxide is -1 , i.e. it is intermediate between the oxidation number of oxygen in water (-2) and in molecular oxygen (0). For this reason, hydrogen peroxide has properties of both an oxidizing and a reducing agent, i.e. exhibits oxidation-reduction duality. Oxidizing properties are nevertheless more characteristic of it because the standard potential of the electrochemical system

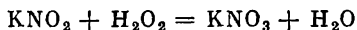


in which H_2O_2 is an oxidizing agent equals 1.776 V, whereas the standard potential of the electrochemical system

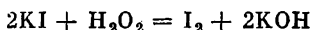


in which hydrogen peroxide is a reducing agent equals 0.682 V. In other words, hydrogen peroxide can oxidize substances for which φ° does not exceed 1.776 V and can reduce only those substances for which φ° is greater than 0.682 V. Table 18 in Vol. 1 (p. 300) shows us that the first group includes much more substances.

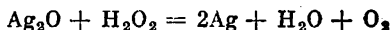
Examples of reactions in which H_2O_2 is an oxidizing agent are the oxidation of potassium nitrite



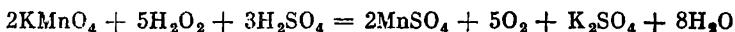
and the separation of iodine from potassium iodide:



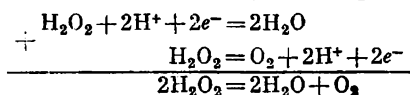
An example of the reducing ability of hydrogen peroxide is the reaction between H_2O_2 and silver(I) oxide:



and also between H_2O_2 and a potassium permanganate solution in an acid medium:



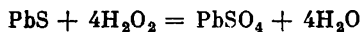
If we add the equations corresponding to the reduction of hydrogen peroxide and to its oxidation, we get an equation of the autoxidation and autoreduction of hydrogen peroxide:



This is the equation of the hydrogen peroxide decomposition process mentioned above.

The use of hydrogen peroxide is associated with its oxidizing ability and with the harmless nature of the product of its reduction (H_2O). It is employed for bleaching fabrics and furs, in medicine (a 3% solution is a disinfecting means), in the food industry (in preserving food products), in agriculture for seed treatment, and also in the production of a number of organic compounds, polymers, and porous materials. It is used in rocket equipment as a strong oxidizing agent.

Hydrogen peroxide is also employed for restoring old paintings in oils that have darkened with time owing to the transformation of white lead into black lead sulphide under the action of the traces of hydrogen sulphide in the air. When such paintings are washed with hydrogen peroxide, the lead sulphide is oxidized to white lead sulphate:



2

THE HALOGENS

The elements fluorine (*Fluorum*), chlorine (*Chlorum*), bromine (*Bromum*), iodine (*Jodum*), and astatine in the main subgroup of Group VII are called the **halogens**. This name, which literally means "salt-forming", was given to the elements for their ability to react with metals to form typical salts, for instance sodium chloride NaCl.

The outer electron layer of halogen atoms has seven electrons—two in the *s* and five in the *p* orbitals (ns^2np^5). The halogens have a considerable affinity to an electron (Table 1)—their atoms readily attach an electron and form singly charged negative ions having the electron configuration of the relevant noble gas (ns^2np^6). The inclination to attach electrons characterizes the halogens as typical non-metals. The analogical structure of the outer electron layer causes great similarity of the halogens to one another, which displays itself both in their chemical properties and in the kinds and properties of the compounds they form. But a comparison of the properties of the halogens shows that there are also appreciable differences between them.

Table 1 gives selected properties of the halogen atoms and the elementary substances they form.

A growth in the atomic number of the elements in the halogen family F to At is attended by an increase in the atomic radii, diminishing of the electronegativity, weakening of the non-metal properties and of the oxidizing power of the elements.

Unlike the other halogens, fluorine is always in the oxidation state -1 in its compounds because it possesses the highest electronegativity of all the elements. The other halogens exhibit various oxidation numbers from -1 to $+7$.

With the exception of several oxides that will be treated below, all the halogen compounds correspond to odd oxidation numbers. This regularity is due to the possibility of consecutive excitation of paired electrons in the atoms Cl, Br, I, and At to the *d* sublevel,

Table 1

Properties of the Halogens*

	Fluorine	Chlorine	Bromine	Iodine	Astatine
Configuration of outer electron layer of atom	$2s^2 2p^5$	$3s^2 3p^5$	$4s^2 4p^5$	$5s^2 5p^5$	$6s^2 6p^5$
Ionization energy of atom, eV	17.42	12.97	11.84	10.45	~9.2
Affinity of atom to electron, eV	3.45	3.61	3.37	3.08	~2.8
Relative electronegativity	4.0	3.0	2.8	2.6	~2.2
Atomic radius, nm	0.064	0.099	0.114	0.133	...
Radius of ion E^- , nm	0.133	0.181	0.196	0.220	0.23
Internuclear distance in molecule E_2 , nm	0.142	0.199	0.228	0.267	...
Standard enthalpy of dissociation of molecules E_2 at 25 °C, kJ/mol	159	243	192	151	109
Physical state in ordinary conditions	Pale greenish gas	Greenish yellow gas	Brownish red liquid	Purplish black crystals	Bluish black crystals
Melting point, °C	-219.6	-101.0	-7.3	113.6	227
Boiling point, °C	-188.1	-34.1	59.2	185.5	317
Degree of thermal dissociation of molecules E_2 :					
at 1000 K	0.043	0.00035	0.0023	0.28	
at 2000 K	0.99	0.37	0.72	0.89	

* The symbol E here and below stands for an atom of the element being considered.

which leads to an increase in the number of electrons participating in the formation of covalent bonds to 3, 5, or 7 (see the diagram in Vol 1, p. 135).

4. Occurrence. Physical Properties

The halogens, owing to their great chemical activity, are found in nature exclusively in a bound state, chiefly as salts of hydrogen halides.

Fluorine is encountered in nature most frequently as the mineral **fluorspar** CaF_2 whose name is due to the fact that its addition to iron ores leads to the formation of low-melting slags in the smelting of iron (the Latin *fluere* means "to flow"). Fluorine is also contained in the minerals **cryolite** Na_3AlF_6 and **fluorapatite** $Ca_5F(PO_4)_3$.

The most important natural compound of chlorine is sodium chloride (table salt) $NaCl$, which is the main starting material for the production of other chlorine compounds. Most of the sodium chloride

in nature is in the water of the seas and oceans. The water in many lakes also contains a considerable amount of NaCl. Examples are the Lakes Elton and Baskunchak in the USSR. Sodium chloride is also encountered in the solid state, forming thick strata of rock salt in the Earth's crust at some places. Other chlorine compounds are also encountered in nature such as potassium chloride in the form of the minerals carnallite $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and sylvite KCl.

Chlorine under a pressure of about 0.6 MPa transforms into a liquid already at room temperature. Liquefied chlorine is usually stored and transported in steel cylinders or tanks.

Like chlorine, bromine occurs mainly in the form of potassium, sodium, and magnesium salts. Metal bromides are contained in sea water, in the water of certain lakes, and in underground brines. In the USSR, the bromine content in underground well water of an industrial significance ranges from 170 to 700 mg/l.

Sea water also contains iodine compounds, but in such minute amounts that their direct extraction from the water is very difficult. There are certain seaweeds, however, that accumulate iodine in their tissues. The ashes of these weeds are the starting material for the production of iodine. Considerable amounts of iodine (from 10 to 50 mg/l) are found in underground well waters. Iodine is also encountered in the form of potassium salts—the iodate KIO_3 and the periodate KIO_4 accompanying deposits of sodium nitrate (saltpetres) in Chile and Bolivia.

Iodine at room temperature has the form of purplish black crystals with a slight lustre. When heated under atmospheric pressure, it sublimes, transforming into a purple vapour. Iodine vapour when cooled crystallizes without passing through the liquid state. This is taken advantage of in practice for purifying iodine from non-volatile admixtures.

The heaviest halogen—astatine—is virtually not found in nature. It is prepared by artificially conducted nuclear reactions. The most long-lived isotope of astatine ^{210}At has a half-life of only 8.3 hours. Negligible amounts of astatine are found in the products of the natural radioactive decay of uranium and thorium.

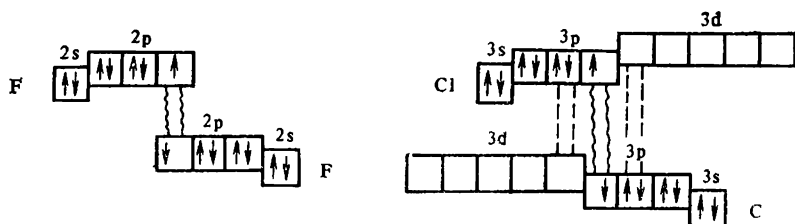
All the halogens have a very sharp odour. Inhaling of even small amounts of them causes great irritation of the respiratory tract and inflammation of the mucous membranes. *Greater amounts of halogens may cause heavy poisoning.*

The molecules of the elementary substances formed by the halogen atoms are diatomic. The increase in the atomic radius in the series F, Cl, Br, I, and At is attended by a growth in the polarizability of the molecules. The result is a greater intermolecular dispersion interaction that underlies an increase in the melting and boiling points of the halogens.

In the series $\text{Cl}_2\text{-Br}_2\text{-I}_2$, the bond strength between the atoms in a

molecule gradually diminishes, which is reflected in diminishing of the enthalpy of dissociation of the molecules E_2 into atoms (Table 1). The explanation is as follows. With an increasing size of the outer electron clouds of the interacting atoms, their overlapping diminishes, while the region of overlapping is farther and farther from the atomic nuclei. Therefore, in going from chlorine to bromine and iodine, the attraction of the halogen atom nuclei to the region of overlapping of the electron clouds diminishes. In addition, in the series Cl-Br-I, the number of intermediate electron layers screening the nucleus grows, which also weakens the interaction of the atomic nuclei with the overlap region.

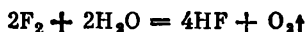
The decreasing of the bond strength in halogen molecules manifests itself in lowering of their heat resistance: the data of Table 1 show that at the same temperature, the degree of thermal dissociation of the molecules increases from Cl_2 to Br_2 and I_2 . But it follows from the same data that fluorine drops out of the general regularity: the strength of the bond between the atoms in its molecule is lower and the degree of thermal dissociation of the molecules is higher than in chlorine. Such anomalous properties of fluorine can be explained by the absence of the d sublevel in the outer electron layer of its atom. A molecule of chlorine and the other halogens has free d orbitals, and therefore additional donor-acceptor interaction strengthening the bond takes place between the atoms. This is shown in the following diagram:



The halogens dissolve comparatively slightly in water. One volume of water at room temperature dissolves about 2.5 volumes of chlorine. This solution is known as chlorine water. When chlorine is passed through water cooled to $0^\circ C$, greenish yellow crystals of the clathrate compound $Cl_2 \cdot 8H_2O$ precipitate from the solution.

The solubility of bromine at $20^\circ C$ is about 3.5 g, and of iodine only 0.02 g per 100 g of water.

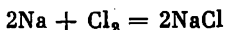
Fluorine cannot be dissolved in water because it vigorously decomposes it:



Bromine and iodine dissolve much better in organic solvents* such as carbon disulphide, ethyl alcohol, diethyl ether, chloroform, and benzene than in water. This is taken advantage of for extracting bromine and iodine from aqueous solutions. If, for example, we agitate an aqueous solution of iodine with a small amount of carbon disulphide (which is immiscible with water), virtually all the iodine will pass from the water into the carbon disulphide, colouring it purple.

5. Chemical Properties

Free halogens exhibit an exceedingly high chemical activity. They react with virtually all elementary substances. They combine with metals especially rapidly, and with the evolution of a large amount of heat. For instance, molten metallic sodium burns in a chlorine atmosphere with a blinding flash, and a white sodium chloride deposit appears on the walls of the vessel:



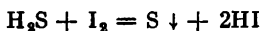
Copper, iron, tin, and many other metals burn in chlorine, forming the relevant salts. Bromine and iodine react with metals in a similar way. In all these cases, the metal atoms give up electrons, i.e. are oxidized, and the halogen atoms attach electrons, i.e. are reduced. This ability of attaching electrons, sharply exhibited in halogen atoms, is their characteristic chemical property. Consequently, halogens are very vigorous oxidizing agents.

The oxidizing properties of halogens also manifest themselves when they react with complex substances. We shall consider several examples.

1. When chlorine is passed through a solution of iron(II) chloride, the latter oxidizes to iron(III) chloride, and the colour of the solution changes from pale green to yellow:



2. If we add hydrogen sulphide water (an aqueous solution of H_2S) to a yellowish aqueous solution of iodine, the liquid loses its colour and becomes turbid owing to the precipitation of sulphur:

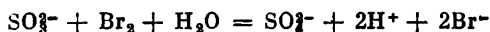


3. When an aqueous solution of bromine is added to a solution of sodium sulphite Na_2SO_3 , the solution loses its colour because the bromine oxidizes the sulphite to sodium sulphate, becoming reduced and transforming into colourless hydrogen bromide. The reaction proceeds with the participation of water molecules and is expressed by the equation



* Fluorine and chlorine react vigorously with many organic solvents.

The net ionic equation is



The chemical activity of fluorine is exceedingly high. As Academician Aleksandr Fersman aptly pointed out, it could be called "all-corroding". The alkali metals, lead, and iron ignite in a fluorine atmosphere at room temperature. Fluorine does not act on some cold metals (Cu, Ni) because a protective fluoride film forms on their surface. When heated, however, fluorine reacts with all metals including gold and platinum.

Fluorine reacts with many non-metals (hydrogen, iodine, bromine, sulphur, phosphorus, arsenic, antimony, carbon, silicon, boron) in the cold state. The reactions proceed with an explosion or with the formation of a flame:

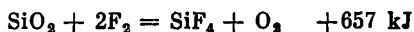


Chlorine, krypton, and xenon combine with fluorine when heated for example:



Fluorine does not react directly only with oxygen, nitrogen, and carbon (in the form of diamond).

Fluorine reacts very vigorously with complex substances. Such stable substances as glass (in the form of wool) and water vapour burn in its atmosphere:



It is interesting to note that oxygen is one of the combustion products.

Free chlorine also displays a very high chemical activity, although the latter is less than that of fluorine. It reacts directly with all the elementary substances except for oxygen, nitrogen, and the noble gases. Such non-metals as phosphorus, arsenic, antimony, and silicon react with chlorine even at a low temperature with the evolution of a large amount of heat. Chlorine reacts quite vigorously with active metals such as sodium, potassium, and magnesium.

Chlorine does not virtually react with hydrogen at room temperature without illumination, but when heated or in bright sunlight the reaction proceeds according to a chain mechanism (see Vol. 1, Sec. 62) with an explosion.

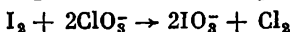
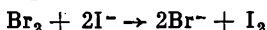
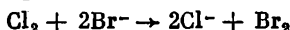
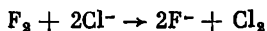
The chemical activity of bromine and iodine is less than that of chlorine, but is nevertheless quite great. They react with many metals and non-metals (for example with phosphorus) in ordinary condi-

tions. Bromine as regards its activity is only slightly inferior to chlorine, whereas iodine differs from it considerably.

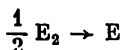
Bromine reacts with hydrogen only when heated. Iodine reacts with hydrogen only with sufficiently great heating and not to the end because the reverse reaction—the decomposition of hydrogen iodide—begins to occur:



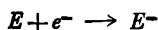
A comparison of the chemical properties of the halogens shows that their oxidizing activity diminishes consecutively from fluorine to astatine. This effect manifests itself in the ability of the lighter halogens in the form of elementary substances to oxidize halide ions of the heavier halogens and in the ability of the latter to reduce the oxygen compounds of the lighter halogens:



Although fluorine has a smaller energy of affinity to an electron than chlorine (see Table 1), it is the strongest oxidizing agent among the halogens. The explanation is as follows. The transformation of gaseous chlorine or fluorine into negatively charged ions can be considered as consisting of two steps—the dissociation of the molecules into individual atoms



and the attachment of an electron to the free halogen atom formed:



The first step of the process requires the expenditure of energy for breaking the bonds between the halogen atoms in a molecule; this energy can be measured by the enthalpy of dissociation of the halogen molecules. For chlorine, consisting of more stable molecules, the enthalpy of dissociation per mole of halogen atoms (121.5 kJ/mol) is considerably higher than for fluorine (79.5 kJ/mol).

The second step of the process is attended by the liberation of energy (affinity to an electron); here the gain in energy for chlorine (348.7 kJ/mol) is somewhat higher than for fluorine (332.7 kJ/mol).

Simple calculations show that the total gain in energy in the above process is higher for fluorine (253.7 kJ/mol) than for chlorine (227.2 kJ/mol), and this characterizes fluorine as a stronger oxidizing agent.

If the reaction proceeds in an aqueous solution, the energy of hydration of the halide ions must be taken into account; with an iden-

tical charge of an ion it is higher when the ionic radius is smaller. Consequently, more energy is evolved in the hydration of the fluoride ion F^- than in the hydration of the chloride ion Cl^- , so that fluorine will also be a stronger oxidizing agent than chlorine in aqueous solutions.

Similar calculations show that upon a transition from chlorine to bromine and iodine the gain in energy in oxidation processes occurring in aqueous solutions with the participation of halogens also diminishes. This is exactly what explains the ability of each halogen to displace heavier halogens in the oxidation state -1 from solutions of their compounds.

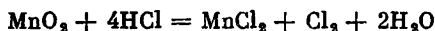
6. Preparation and Uses

Natural compounds contain halogens (with rare exceptions) in the form of negatively charged ions. For this reason, almost all the ways of preparing free halogens consist in oxidation of their ions. This is achieved either with the aid of oxidizing agents, or by the action of an electric current.

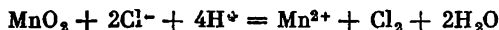
Fluorine, owing to its high electronegativity, can be separated from its compounds only by electrolysis. It was first prepared in 1886 by decomposing a mixture of anhydrous liquid hydrogen fluoride with KF using an electric current. This method is used at present for the industrial preparation of fluorine. A melt having the composition $KF + 2HF$ (melting point $70^\circ C$) is subjected to electrolysis. The latter is conducted in a nickel vessel that is the cathode, and carbon is the anode. The cathode and anode spaces are separated by a membrane to prevent an explosion that would otherwise occur upon mixing of the electrolysis products—hydrogen and fluorine.

Chlorine is produced at present in large amounts by the electrolysis of aqueous solutions of sodium or potassium chloride. Chlorine is liberated at the anode, and sodium or potassium hydroxide (depending on the salt used) is formed at the cathode (see Sec. 83).

In laboratories, chlorine is prepared by acting on hydrogen chloride with various oxidizing agents. We shall remind our readers, for example, of the laboratory method of preparing chlorine by reacting manganese dioxide with hydrochloric acid known from school days:



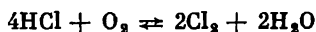
This reaction is expressed by the following net ionic equation:



which shows that here chloride ions Cl^- are oxidized into chlorine atoms (which then form Cl_2 molecules) and the manganese in the MnO_2 is reduced to an oxidation state of $+2$ (the Mn^{2+} ions). Chlorine was first prepared by the Swedish chemist Karl Scheele in 1774 with the aid of this reaction.

Chlorine can be prepared in a similar way from hydrochloric acid by acting on it with such oxidizing agents as PbO_2 , KClO_3 , and KMnO_4 .

Oxygen in ordinary conditions does not react with HCl to any appreciable extent. But if HCl and O_2 are passed through a tube heated to 400°C and containing pieces of pumice on which copper(II) chloride CuCl_2 is distributed as a catalyst, the hydrogen chloride is oxidized by the oxygen



the yield of chlorine reaching 80%. This reaction was previously used for the industrial production of chlorine.

Bromine and iodine can be prepared similarly to chlorine by oxidizing HBr and HI with a variety of oxidizing agents. They are generally produced on a commercial scale from bromides and iodides by acting with chlorine on their solutions. Hence, the preparation of bromine and iodine is also based on the oxidation of their ions, chlorine being used as the oxidizing agent.

In the USSR, bromine is chiefly extracted from underground well water, and also from the "brine" (saturated solution) of certain saline lakes.

Iodine is mainly produced in the USSR from underground well water.

The halogens, especially chlorine, find wide application in the chemical industry.

Fluorine is employed for preparing some valuable hydrocarbon fluoroderivatives having unique properties, for instance lubricants withstanding a high temperature, a plastic stable to chemical reagents (Teflon—polytetrafluoroethylene), liquids for refrigerating machines (Freons or Khladons).

Chlorine is used for preparing a multitude of inorganic and organic compounds. It is employed in the production of hydrogen chloride, chlorinated lime, hypochlorites, chlorates, etc. A great amount of chlorine is used for bleaching fabrics and the pulp intended for the production of paper. Chlorine is also used for the sterilization of potable water and the disinfection of sewage. In non-ferrous metallurgy, it is used for the chlorination of ores, which is one of the stages in the production of certain metals.

Especially great significance has been acquired lately by various chlorinated organic products. Chlorine-containing organic solvents, for example, dichloroethane and carbon tetrachloride, find great use for extracting fats and degreasing metals. Some chlorine-containing organic products are effective means of combatting agricultural pests. Others are the basis for manufacturing various plastics, synthetic fibres, artificial rubbers, and leather substitutes (Pavinol). The development of engineering is accompanied by expansion of the

field of application of chlorine-containing organic products. The result is a continuous increase in the production of chlorine.

The widespread use of chlorine in various branches of the national economy, and also the scale of its production and use make it possible to relate chlorine, in addition to sulphuric acid, ammonia, and soda, to the most important products manufactured by the chemical industry.

Bromine is needed for the production of a variety of medicines, certain dyes, and also of silver bromide used in the manufacture of photographic materials.

Iodine is used in medicine in the form of tincture of iodine (a 10% solution of iodine in ethyl alcohol), which is an excellent antiseptic and hemostatic agent. Iodine is also included in the composition of a number of pharmaceutical preparations.

7. Hydrogen Halides

Hydrogen halides and their salts are of the greatest significance among the halogen compounds.

Molecules of hydrogen halides have polar covalent bonds: the shared electron pair is shifted towards the halogen atom, which has a higher electronegativity. Selected properties of the hydrogen halides are given in Table 2.

Table 2

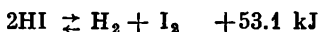
Selected Properties of Hydrogen Halides

	HF	HCl	HBr	HI
Standard Gibbs energy of formation at 25 °C, kJ/mol	-272.8	-95.2	-53.3	+1.8
Standard enthalpy of formation at 25 °C, kJ/mol	-270.7	-92.3	-36.3	+26.6
Standard enthalpy of dissociation into atoms at 25 °C, kJ/mol	565.7	431.6	364.0	298.3
Internuclear distance in molecule, nm	0.092	0.127	0.141	0.161
Dipole moment of molecule, D	1.91	1.03	0.79	0.42
Melting point, °C	-83.4	-114.2	-86.9	-50.8
Boiling point, °C	19.5	-85.1	-66.8	-35.4
Solubility in water at 10 °C, mol/l*	Unlimited	14	15	12
Degree of thermal dissociation:				
at 300 °C	—	3×10^{-9}	3×10^{-5}	0.19
at 1000 °C	—	1.4×10^{-4}	0.005	0.33

* These data relate to liquid HF and gaseous HCl, HBr, and HI with their partial pressure equal to standard atmospheric pressure.

The strength of the chemical bond in hydrogen halide molecules diminishes regularly in the series HF-HCl-HBr-HI. This manifests itself in the change in the enthalpy of dissociation of the molecules into atoms (Table 2). The bond weakens here for the same reasons that were considered in comparing the stability of free halogen molecules (p. 20). As shown by the diagram in Fig. 3, when going, for instance, from HF to HI, the degree of overlapping of the electron clouds in the hydrogen and halogen atoms diminishes, while the overlap region is at a greater distance from the halogen atom nucleus and is screened more strongly by the growing number of intermediate electron layers. In addition, in the series F-Cl-Br-I, the electronegativity of the halogen atom diminishes. For this reason, in the HF molecule the electron cloud of the hydrogen atom is shifted towards the halogen atom to the greatest extent, and in the molecules HCl, HBr, and HI to a smaller and smaller extent. This also leads to diminishing of the overlapping of the interacting electron clouds and, consequently, to weakening of the bond between the atoms.

Decreasing of the bond strength in hydrogen halide molecules is attended by lowering of their stability to heating. Thermal dissociation of hydrogen fluoride occurs only at very high temperatures (over 3500 °C), whereas hydrogen iodide already at 300 °C decomposes considerably into iodine and hydrogen:



All hydrogen halides are colourless gases having a pungent odour.

The hydrogen halides are very well soluble in water. At 0 °C, one volume of water dissolves about 500 volumes of HCl, 600 volumes of HBr, and about 425 volumes of HI (at 10 °C). Hydrogen fluoride mixes with water in any proportions.

The dissolution of hydrogen halides is accompanied by their dissociation according to the acid type. Only hydrogen fluoride dissociates comparatively slightly, while the other hydrogen halides are among the strongest acids.

Concentrated solutions of hydrogen halides fume in air owing to the evolution of hydrogen halides forming a mist with the water vapour contained in the air. This mist consists of minute droplets of the relevant acids.

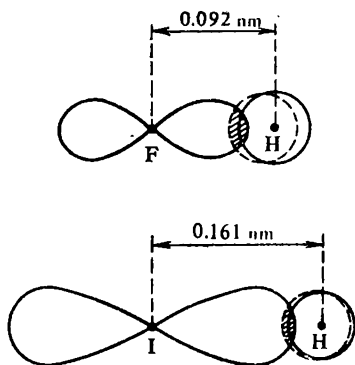


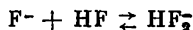
Fig. 3. Overlapping of the electron clouds in the formation of HF and HI molecules

The dash line conditionally shows the shifting of the hydrogen atom electron cloud towards the halogen atom

The boiling and melting points in the series HI-HBr-HCl change quite regularly (Table 2), whereas they sharply grow when passing over to HF . As we have mentioned in Vol. 1, Sec. 47, this is due to the association of the hydrogen fluoride molecules because of the appearance of hydrogen bonds between them. Determination of the vapour density shows that near the boiling point gaseous hydrogen fluoride consists of aggregates having the average composition $(\text{HF})_4$. Upon further heating, these aggregates gradually decompose, but only at about 90°C does gaseous HF consist of simple molecules.

When dissolved in water, hydrogen fluoride molecules dissociate with the formation of H^+ and F^- ions. The hydrogen bonds partly break so that the dissociation of HF into ions requires a considerable expenditure of energy. This is why hydrogen fluoride dissociates in aqueous solutions to a considerably smaller extent than the other hydrogen halides: the dissociation constant of hydrogen fluoride is 7×10^{-4} , so that this acid is only slightly superior to acetic acid in its strength.

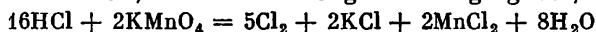
The F^- ions appearing in the dissociation of HF are bound to a considerable extent to undissociated HF molecules to form the HF_2^- ion in which the fluorine atoms are bound to each other by a hydrogen bond:



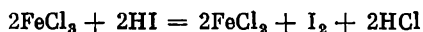
Consequently, when hydrogen fluoride is neutralized, acid salts first appear such as KHF_2 .

The negative ions of the hydrogen halides except for the fluoride ion have reducing properties that increase from Cl^- through Br^- to I^- .

The chloride ion is oxidized by fluorine, potassium permanganate, manganese dioxide, and other strong oxidizing agents, for example:

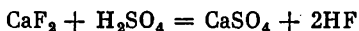


Bromide and especially iodide ions are oxidized still more readily. The latter are also easily oxidized by bromine, nitrates, and salts of Fe(III) , for instance:



Since halide ions possess reducing properties, when hydrogen halides act on metals the latter can be oxidized only by the hydrogen ions H^+ . Hence, hydrogen halides can react in solution only with the metals preceding hydrogen in the electromotive series.

A solution of hydrogen fluoride in water is called **hydrofluoric acid**. Hydrogen fluoride is usually produced from fluorite CaF_2 by reacting it with concentrated sulphuric acid:

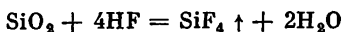


A commercial solution of hydrogen fluoride usually contains 40% of HF . Hydrogen fluoride reacts with most metals. In many

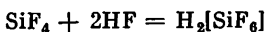
cases, however, the salt formed is only slightly soluble, owing to which a protective film is formed on the surface of the metal. Lead, particularly, behaves in this way, which underlies its use for the fabrication of apparatus stable to the action of HF.

Most fluorides—the salts of hydrogen fluoride—are slightly soluble in water; only the fluorides of Na, K, Al, Sn, and Ag are well soluble. *All fluorides are poisonous.*

A remarkable property of hydrogen fluoride and hydrofluoric acid is their ability to react with silicon dioxide SiO_2 present in glass. The product is gaseous silicon tetrafluoride SiF_4 :



Silicon tetrafluoride is not evolved in a solution of hydrofluoric acid because it reacts with HF molecules to form the well soluble complex fluosilicic acid:



The reaction of HF with silicon dioxide underlies the use of hydrofluoric acid for etching various marks, inscriptions, and illustrations on glass.

Since hydrogen fluoride destroys glass, it is stored in the laboratory in vessels made from special kinds of plastics. It can also be stored in lead vessels or in glass vessels coated inside with a paraffin layer.

The applications of hydrogen fluoride are quite diverse. Anhydrous HF is chiefly used in organic synthesis, while hydrofluoric acid is employed in the production of fluorides, the etching of glass, the removal of sand from metal castings, and in the analysis of minerals.

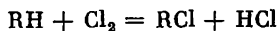
Hydrogen fluoride vapour is very poisonous. If concentrated hydrofluoric acid gets onto the skin, it causes severe burns.

Hydrochloric acid is prepared by dissolving hydrogen chloride in water. At present, the main method of the industrial manufacture of hydrogen chloride is its synthesis from hydrogen and chlorine:



This process is conducted in special plants in which a mixture of hydrogen and chlorine is continuously formed and immediately burns in a uniform flame. This results in a quiet (without an explosion) reaction. The starting materials for the production of hydrogen chloride are the chlorine and hydrogen produced in the electrolysis of an NaCl solution (Sec. 83).

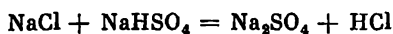
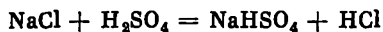
Large amounts of HCl are also produced as a by-product in the chlorination of organic compounds:



where R is an organic radical.

Hydrochloric acid is a colourless liquid with a pungent odour. Concentrated hydrochloric acid usually contains about 37 % of HCl. Its density is 1.19 g/cm³.

The former "sulphate" method of producing HCl, which at present is employed only in laboratories, is based on the reaction of NaCl with concentrated H₂SO₄ according to the equations:



The first of these reactions proceeds to a considerable extent with slight heating; the second one occurs only at higher temperatures. Sodium sulphate Na₂SO₄ is obtained as a by-product.

When a concentrated hydrogen chloride solution is heated, first hydrogen chloride evaporates together with a small amount of water. This occurs until the residue is a 20.2% solution. The latter is distilled without any change in composition at a constant temperature of 110 °C. Conversely, if a dilute HCl solution is heated, water mainly evaporates. When the concentration of the HCl in the residue reaches 20.2%, the liquid begins to distill without any change in composition, as in the preceding case. Such solutions, characterized by an identical composition of the liquid and saturated vapour, and therefore distilling without a change in their composition, are called **constant boiling** or **azeotropic mixtures**.

Like other strong acids, HCl vigorously reacts with many metals and metal oxides. Its salts are called **chlorides**. Most of them are well soluble in water. The slightly soluble ones are AgCl, PbCl₂, CuCl, and Hg₂Cl₂.

Hydrochloric acid is one of the most important acids in chemical practice. Millions of tonnes of this acid are produced in the world every year. Many of its salts also find wide application. We shall note the most important of the chlorides.

Sodium chloride NaCl, or **table salt**, is the starting material for the production of chlorine, hydrogen chloride, sodium hydroxide, and sodium carbonate (soda). It is used in the dye, soap, and many other industries. It is also used as a food seasoning and preservative.

Potassium chloride KCl is used in great amounts in agriculture as a fertilizer.

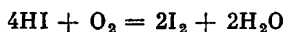
Calcium chloride CaCl₂·6H₂O is employed to prepare refrigerants. Anhydrous CaCl₂ is widely used in laboratory practice for drying gases and dehydrating liquid organic substances.

Mercury (II) chloride HgCl₂, or **corrosive sublimate**, is a very strong poison. Dilute solutions of corrosive sublimate (1 : 1000) are used in medicine as strong disinfectants (see also p. 298).

Silver chloride AgCl is the least soluble salt of hydrochloric acid. The precipitation of AgCl when Cl⁻ ions react with Ag⁺ ions is a

characteristic reaction for chloride ions. Silver chloride is used in photography to manufacture light-sensitive materials.

Hydrogen bromide and **hydrogen iodide** are very similar in their properties to hydrogen chloride, but differ in having more expressed reducing properties. Molecular oxygen gradually oxidizes hydrogen iodide even at room temperature. The rate of the reaction greatly increases under the action of light:

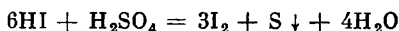


Hydrogen bromide reacts with oxygen much more slowly, while in ordinary conditions hydrogen chloride does not react with it at all.

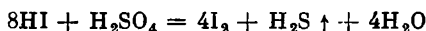
The reducing properties of hydrogen bromide and hydrogen iodide manifest themselves quite appreciably in their reaction with concentrated sulphuric acid. Here HBr reduces H_2SO_4 to SO_2 :



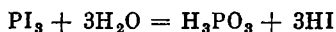
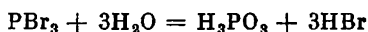
while HI reduces it to free sulphur or even to H_2S :



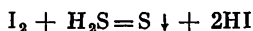
or



This is why it is difficult to prepare HBr and virtually impossible to prepare HI by reacting sulphuric acid with bromides or iodides. These hydrogen halides are usually produced by reacting water with phosphorus compounds of bromine and iodine— PBr_3 and PI_3 . The latter become completely hydrolyzed, forming phosphorous acid and the relevant hydrogen halide:



A solution of hydrogen iodide (up to a 50% concentration) can be obtained by passing H_2S into an aqueous suspension of iodine. The reaction proceeds according to the equation:



The salts of hydrogen bromide and hydrogen iodide are called **bromides** and **iodides**, respectively. The solubility of bromides and iodides in the majority of cases is similar to that of the relevant chlorides.

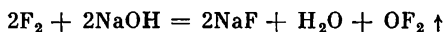
Solutions of sodium and potassium bromides are used in medicine as tranquilizers in nervous disorders. Silver bromide is used in large amounts in the manufacture of photographic materials. Potassium iodide is used in medicine, in particular to cure diseases of the endocrine system.

8. Oxygen Compounds

The halogens form a number of compounds with oxygen. All these compounds, however, are not stable and are not obtained in the direct reaction of halogens with oxygen. These features of the oxygen-containing halogen compounds agree with the fact that almost all of them are characterized by positive values of the standard Gibbs energy of formation (see, for example, Table 7 in Vol. 1, p. 213, the values of ΔG_{298}° for ClO_2 , Cl_2O , Cl_2O_7 , and OF_2).

The most stable of the oxygen compounds of the halogens are the salts of the oxyacids, and the least stable are the oxides and acids. The halogens, except for fluorine, in all their oxygen compounds exhibit a positive oxidation number reaching seven.

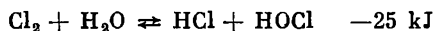
Oxygen difluoride can be prepared by passing fluorine into a cooled 2% solution of NaOH. The following reaction occurs:



Oxygen, ozone, and hydrogen peroxide are always formed in addition to the OF_2 . In ordinary conditions, OF_2 is a colourless gas with a sharp odour of ozone. Oxygen difluoride is very poisonous, has strong oxidizing properties, and can be used as an effective oxidizing agent of rocket fuels.

Chlorine has the most numerous and practically important oxygen compounds, and we shall treat them in somewhat greater detail.

We have already mentioned that the oxygen compounds of chlorine can be prepared only indirectly. We shall begin our discussion of how they are formed with the process of chlorine hydrolysis, i.e. with the reversible reaction between chlorine and water



as a result of which hydrogen chloride and **hypochlorous acid** HOCl are formed.

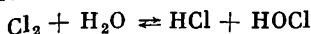
The hydrolysis of chlorine is an autoxidation-autoreduction reaction in which one of the chlorine atoms attaches an electron from the other atom and is reduced, while the other atom of chlorine is oxidized.

The HCl and HOCl obtained in the hydrolysis of chlorine can react with each other, again forming chlorine and water, consequently, the reaction does not proceed to the end. Equilibrium sets in when about one-third of the dissolved chlorine reacts. Hence, chlorine water always contains an appreciable amount of hydrogen chloride and hypochlorous acid in addition to Cl_2 molecules.

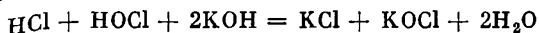
Hypochlorous acid HOCl is a very weak acid ($K = 5 \times 10^{-8}$). It is weaker than carbonic acid. Its salts are called **hypochlorites**. Being a very unstable compound, hypochlorous acid gradually decomposes even in a dilute solution (see below).

Hypochlorous acid is a very strong oxidizer. Its formation when chlorine reacts with water explains the bleaching properties of chlorine. Absolutely dry chlorine does not bleach, but in the presence of moisture, the hypochlorous acid formed in the hydrolysis of the chlorine rapidly destroys pigments.

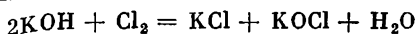
If an alkali is added to chlorine water, the neutralization of the hypochlorous acid and hydrogen chloride results in shifting of the equilibrium in the system



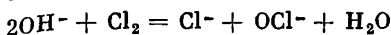
to the right; the reaction proceeds virtually to the end, and a solution is obtained containing a hypochlorite and a chloride:



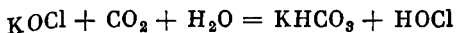
The same occurs if chlorine is passed directly into a cold solution of an alkali:



The net ionic equation is



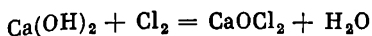
The hypochlorite and chloride solution obtained in this way is used for bleaching. Its bleaching properties are due to the fact that potassium hypochlorite readily decomposes when acted upon by the carbon dioxide contained in the air, hypochlorous acid being formed:



It is this acid that bleaches pigments by oxidizing them

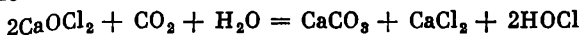
A similar solution containing sodium hypochlorite is obtained when chlorine is passed into a sodium hydroxide solution. Both solutions can be prepared by the electrolysis of potassium or sodium chloride solutions if the evolving chlorine is allowed to react with the alkalis formed in electrolysis (see p. 235).

When chlorine reacts with dry slaked lime, **lime chloride** or **chlorinated lime** is obtained. Its main constituent part is the salt CaOCl_2 formed according to the equation:

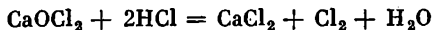


This salt, which is often written in the form CaCl(OCl) , has the structural formula $\text{Ca} \begin{array}{l} \text{OCl} \\ \diagup \quad \diagdown \\ \text{Cl} \end{array}$, according to which it should be considered as a mixed salt of hydrochloric and hypochlorous acids.

Chlorinated lime is a white powder with a sharp odour and has strong oxidizing properties. In humid air, it gradually decomposes under the action of carbon dioxide, liberating hypochlorous acid:

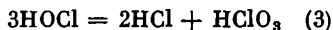
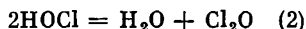


When chlorinated lime is reacted with hydrochloric acid, chlorine is evolved:



Chlorinated lime is used for bleaching vegetable fibres (fabrics, paper), and for disinfection.

In solution, hypochlorous acid experiences three different kinds of transformations that proceed independently of one another:



By changing the conditions, the reaction can be made to proceed virtually completely in any one given direction.

Under the action of direct sunlight and in the presence of certain catalysts or reducing agents, hypochlorous acid decomposes according to Eq. (1).

Reaction (2) occurs in the presence of dehydrating substances such as CaCl_2 . The reaction yields **chlorine(I) oxide (hypochlorous anhydride)** Cl_2O that is an extremely unstable yellow-brown gas having an odour like that of chlorine.

Hypochlorous acid decomposes especially easily by reaction (3) when heated. Therefore, if chlorine is passed into a *hot* solution of potassium hydroxide, KClO_3 is obtained directly instead of KOCl :



The products are potassium chloride and potassium **chlorate**, a salt of **chloric acid** HClO_3 . Since the potassium chlorate is poorly soluble in cold water, it precipitates when the solution is cooled.

Chloric acid corresponding to the chlorates is known only in the form of an aqueous solution with a concentration of not over 50%. It exhibits properties of a strong acid (approximately equal in strength to HCl and HNO_3) and a strong oxidizing agent. For example, its concentrated solutions ignite wood.

Unlike free HClO_3 , the oxidizing properties of the chlorates in solution are expressed weakly. Most of them are well soluble in water; *all of them are poisonous*. Potassium chlorate KClO_3 has found the greatest application among the chlorates. It readily decomposes when heated. In the presence of MnO_2 (as a catalyst), it mainly decomposes according to the equation:



The salt KClO_3 forms mixtures with various combustible substances (sulphur, carbon, phosphorus) that explode upon an impact. This underlies its use in artillery (the making of igniting fuses). Potassium chlorate is used in pyrotechnics to prepare Bengal lights and

other easily igniting mixtures. But the main consumer of potassium chlorate is the match industry. The head of an ordinary match contains about 50% of KClO_3 .

The anhydride of chloric acid is not known. When KClO_3 is acted upon by concentrated sulphuric acid, a yellow-brown gas with a characteristic odour, **chlorine dioxide** ClO_2 , is liberated instead of the anhydride. Chlorine dioxide is a very unstable compound that readily decomposes with an explosion into chlorine and oxygen when heated, struck, or brought into contact with combustible substances.

Chlorine dioxide is employed for bleaching or sterilizing a variety of materials (paper pulp, flour, etc.).

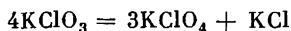
When ClO_2 reacts with a solution of an alkali, the following reaction proceeds at a slow rate:



with the formation of salts of two acids—chloric HClO_3 and **chlorous** HClO_2 .

Chlorous acid has a low stability. It is intermediate between HOCl and HClO_3 in its strength and oxidizing activity. Its salts—**chlorites**—are used for bleaching fabrics.

When potassium chlorate is carefully heated without a catalyst, its decomposition mainly follows the reaction



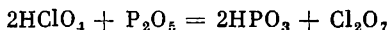
The **potassium perchlorate** KClO_4 formed is very poorly soluble in water, and can therefore be separated quite easily.

The action of concentrated sulphuric acid on KClO_4 produces free **perchloric acid** HClO_4 —a colourless liquid fuming in the air.

Anhydrous HClO_4 has a low stability and sometimes explodes when stored, but its aqueous solutions are quite stable. The oxidizing properties of HClO_4 are weaker than those of HClO_3 , while its acid properties are stronger. Perchloric acid is the strongest of all known acids.

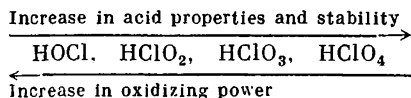
The salts of HClO_4 , with a few exceptions including KClO_4 , are well soluble and do not exhibit oxidizing properties in solution.

If perchloric acid is heated with P_2O_5 that removes water from it, the products include **dichloride heptoxide** or **perchloric anhydride** Cl_2O_7 :



Dichloride heptoxide is an oily liquid boiling with decomposition at 80°C . When subjected to a blow or strong heating, Cl_2O_7 explodes.

The change in the properties in the oxyacid series of chlorine can be expressed by the following scheme:



A growth in the oxidation number of chlorine is attended by an increase in the stability of its oxyacids and by weakening of their oxidizing power. Hypochlorous acid is the strongest oxidizing agent, and perchloric acid is the weakest one.

Conversely, the strength of the oxyacids of chlorine increases with a growth in its oxidation number. Of all the chlorine hydroxides, the weakest is hypochlorous acid and the strongest, perchloric acid. Such a regularity—an increase in the acid properties of a hydroxide (and, correspondingly, weakening of its basic properties) with a growth in the oxidation number is characteristic not only of chlorine, but also of other elements. This regularity can be explained in a first approximation by considering all the chemical bonds in hydroxide molecules as purely ionic ones.

Figure 4 schematically shows a portion of the hydroxide molecule $E(OH)_n$ consisting of an n -charged ion E^{n+} , an oxygen ion O^{2-} and a hydrogen ion (proton) H^+ . Dissociation of this portion of the molecule into ions may occur either with breaking of the $E-O$ bond (as a result of which an OH^- ion becomes detached), or with breaking of the $O-H$ bond (as a result of which the H^+ ion becomes detached). In the first case, the hydroxide will exhibit the properties of a base, and in the second, of an acid.

Each of the possible ways of hydroxide dissociation will be followed the easier, the weaker is the bond between the relevant ions. When the oxidation number of the element E grows, the charge of the E^{n+} ion increases, which makes its attraction to the O^{2-} ion stronger and thus hinders base-type dissociation of the hydroxide. At the same time, the mutual repulsion of the identically charged E^{n+} and H^+ ions grows, which promotes acid-type dissociation. Thus, *an increase in an element's oxidation number is attended by a growth in the acid properties and weakening of the basic properties of the hydroxide formed by this element.*

An increase in the radius of the E^{n+} ion with its charge remaining constant leads to a growth in the distances between the centre of this ion and those of the O^{2-} and H^+ ions. The result will be weaker mutual electrostatic attraction of the E^{n+} and O^{2-} ions, which facilitates base-type dissociation. Simultaneously, the mutual repulsion of the E^{n+} and H^+ ions will diminish, so that acid-type dissociation is hampered. Consequently, *an increase in an element's ionic radius (at a constant charge) is attended by a growth in the basic properties and weakening of the acid properties of the hydroxide formed by this element.* An example of this regularity is the

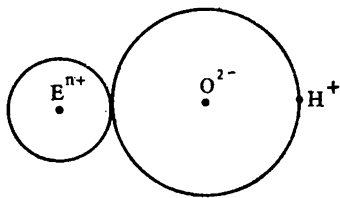
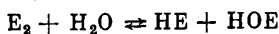


Fig. 4. An ionic scheme of a hydroxide molecule $E(OH)_n$

change in the acid dissociation constants in the series HOCl ($K = 5 \times 10^{-8}$), HOBr, ($K = 2 \times 10^{-9}$), and HOI ($K = 2 \times 10^{-10}$).

Naturally, the assumption on the purely ionic nature of the chemical bonds in hydroxide molecules is a quite rough one. Actually, the O—H bond is chiefly covalent, while the E—O bond may be considered close to an ionic one only for the alkali metals. In addition, the above interpretation of the acid and basic properties of hydroxides does not take into account the features of interaction of the EO^- , H^+ , E^{n+} , and OH^- ions with molecules of the solvent (water). Hence, the scheme showing how the charge and size of the E^{n+} ion affect the nature of dissociation of the molecule $\text{E}(\text{OH})_n$ cannot be the basis for a quantitative assessment of the acid and basic properties of hydroxides. This scheme in the majority of cases leads to proper qualitative conclusions, however, when comparing the acid and basic properties of the various hydroxides formed by a given element in different oxidation states, or when comparing the properties of similar hydroxides formed by elements of the same subgroup of the periodic table.

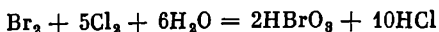
Oxygen Compounds of Bromine and Iodine. Solutions of hypobromous (HOBr) and hypoiodous (HOI) acids can be obtained, like ones of hypochlorous acid, by reacting the relevant halogen with water, respectively:



equilibrium shifting more and more to the left in the series Cl_2 - Br_2 - I_2 .

The stability and oxidizing activity of the acids diminish in the series HOCl, HOBr, HOI. The acid properties (see above) also weaken accordingly. Hypoiodous acid HOI is already an amphoteric compound whose basic properties predominate somewhat over its acid ones.

Bromic (HBrO_3) and **iodic** (HIO_3) acids can be prepared by oxidizing bromine or iodine water with chlorine:



Bromic acid is very similar in its properties to HClO_3 , whereas the oxidizing and acid properties of HIO_3 are expressed considerably more weakly.

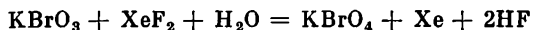
Iodic acid has the form of colourless crystals quite stable at room temperature. When carefully heated to 200°C , a powder of diiodine pentoxide or iodic anhydride I_2O_5 can be obtained:



Diiodine pentoxide displays oxidizing properties, while when heated to above 300°C , it decomposes into iodine and oxygen.

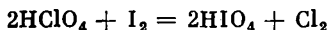
Until recently, bromine was believed to form no compounds in which its oxidation state is seven. In 1968, however, **perbromates**

and **perbromic acid** HBrO_4 corresponding to them were prepared by oxidizing KBrO_3 . Xenon difluoride XeF_2 was found to be the best oxidizer:

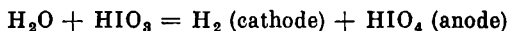


Very little is known to date about the properties of perbromic acid and its salts. Conversely, **periodic acid** (HIO_4) and its salts (**periodates**) have been studied quite well.

The acid itself can be prepared by reacting iodine with HClO_4 :



or by the electrolysis of a solution of HIO_3 :



Periodic acid separates from the solution as colourless crystals of the composition $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$. This hydrate should be considered as the pentabasic acid H_5IO_6 (**ortho-iodic**) because all the five hydrogen atoms in it can be displaced by metals with the formation of salts (for instance, Ag_5IO_6). Periodic acid is weak, but it is a stronger oxidizing agent than HClO_4 .

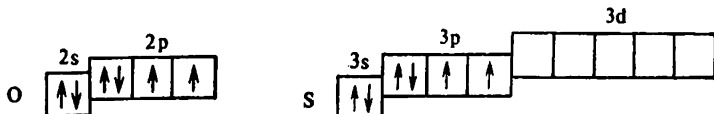
Diiodine heptoxide I_2O_7 has not been obtained.

3

THE MAIN SUBGROUP OF GROUP SIX

The main subgroup of group six of the periodic table includes **oxygen, sulphur, selenium, tellurium, and polonium**. The latter is a radioactive metal; both natural and artificially prepared isotopes of it are known.

The atoms of the elements being considered have six electrons in their outer electron shell—two in the *s* orbital and four in the *p* orbital. The oxygen atom differs from the atoms of the other elements of the subgroup in the absence of a *d* sublevel in the outer electron layer:



As indicated in Vol. 1, p. 134, such an electron configuration of the oxygen atom results in great expenditures of energy for “unpairing” its electrons that are not compensated by the energy of formation of new covalent bonds. Consequently, the covalence of oxygen, as a rule, is two. Sometimes, however, the oxygen atom, having unshared electron pairs, can play the role of a donor of electrons and form additional covalent bonds in the donor-acceptor way.

In sulphur and the remaining elements of the subgroup, the number of unpaired electrons in an atom can be increased by transferring the *s* and *p* electrons to the *d* sublevel of the outer layer. In this connection, these elements exhibit a covalence equal not only to two, but also to four and six.

All the elements of the given subgroup except polonium are non-metals, although they are less active than the halogens. They display both negative and positive oxidation states. In compounds with metals and hydrogen, their oxidation number, as a rule, is -2 . In compounds with non-metals, for example with oxygen, it can

be +4 or +6. An exception here is oxygen itself. In the magnitude of its electronegativity, it is inferior only to fluorine (see Table 6 in Vol. 1, p. 129); therefore, its oxidation state is positive (+2) only in its compound with this element (OF_2). The oxidation state of oxygen is negative in its compounds with all other elements and is generally -2 . In hydrogen peroxide and its derivatives (see Sec. 3) it is -1 .

As in the halogen group, the physical and chemical properties of the elements being considered change regularly with an increase in their atomic number. The appearance of new electron layers leads to an increase in the atomic radii, diminishing of the electronegativity, lowering of the oxidation activity of the uncharged atoms, and to an increase in the reducing properties of the atoms having an oxidation number of -2 . Consequently, the non-metallic properties vividly expressed in oxygen are weakened very much in tellurium.

Table 3 contains selected properties of the elements of the main subgroup of Group VI (except for polonium).

Table 3

Selected Properties of Oxygen and Its Analogues

	Oxygen	Sulphur	Selenium	Tellurium
Configuration of outer electron layer of atom	$2s^2 2p^4$	$3s^2 3p^4$	$4s^2 4p^4$	$5s^2 5p^4$
Ionization energy of atom, eV	13.62	10.36	9.75	9.01
Relative electronegativity	3.50	2.6	2.5	2.1
Atomic radius, nm	0.066	0.104	0.117	0.137
Radius of ion E^{2-} , nm	0.136	0.182	0.193	0.211
Melting point, $^{\circ}\text{C}$	-218.8	119.3^*	217^{**}	449.8^{**}
Boiling point, $^{\circ}\text{C}$	-183.0	444.6	685	990

* The monoclinic modification; the melting point of the rhombic modification is 112.8°C .

** The trigonal modification.

OXYGEN [OXYGENIUM]

9. Oxygen in Nature. Air

Oxygen is the most abundant element in the Earth's crust. The atmospheric air contains it in the free state, while water, minerals, rock, and all the substances which the organisms of plants and animals are built of contain it in the combined state. The overall amount of oxygen in the Earth's crust is close to half of its total mass (47%).

Natural oxygen consists of three stable isotopes: ^{16}O (99.76 %), ^{17}O (0.04 %), and ^{18}O (0.2 %).

Atmospheric air is a mixture of many gases. In addition to oxygen and nitrogen forming the bulk of air, it includes small amounts of the noble gases, carbon dioxide, and water vapour. It also contains a certain amount of dust and random impurities. Oxygen, nitrogen, and the noble gases are considered to be constant constituents of air because their content in it is the same virtually everywhere. The content of carbon dioxide, water vapour, and dust, however, may vary depending on the local conditions.

Carbon dioxide is formed in nature in the burning of wood and coal, the breathing of animals, and in decay. An especially great amount of CO_2 is discharged into the atmosphere in large industrial centres as a product of combustion of enormous amounts of fuel.

At some places on the Earth, CO_2 is released into the air owing to volcanic activity, and also from underground sources. Notwithstanding the continuous evolution of carbon dioxide into the atmosphere, its content in the air is quite constant, forming on an average about 0.03 % (vol). The explanation is the absorption of CO_2 by plants, and also its dissolution in water.

Water vapour may be present in the air in various amounts from fractions of a per cent to several per cent, depending on the local conditions and the temperature.

The **dust in the air** consists mainly of minute particles of the minerals forming the Earth's crust, coal particles, plant pollen, and also various bacteria. The amount of dust in the air varies quite considerably: it is lesser in cold weather and greater in warm weather. After a rainfall, the air becomes cleaner because the raindrops carry along the dust.

Finally, the random impurities of the air include substances such as hydrogen sulphide and ammonia liberated in the decay of organic remains, sulphur dioxide SO_2 produced in the roasting of sulphurous ores or in the combustion of coal containing sulphur, and nitrogen oxides formed upon electrical discharges in the atmosphere. These impurities are usually encountered in negligible amounts and are constantly removed from the air, dissolving in rain water.

If we take into consideration only the constant constituent parts of air, its composition can be expressed by the data given in Table 4.

The mass of one litre of air at 0°C and standard atmospheric pressure is 1.293 g. At a temperature of -140°C and a pressure

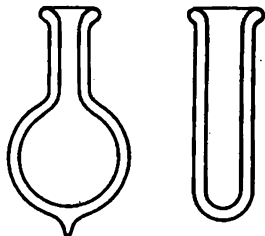


Fig. 5. Dewar flasks (cross section)

Table 4
Composition of Air

Constituent part of air	Content, %	
	by volume	by mass
Nitrogen	78.2	75.5
Oxygen	20.9	23.2
Noble gases	0.9	1.3

of about 4 MPa, air condenses into a colourless transparent liquid.

Notwithstanding its low boiling point (about -190°C) at atmospheric pressure, liquid air can be stored for quite a long time in Dewar flasks—glass vessels with at least two walls that have the space between the walls evacuated (Fig. 5).

Ethyl alcohol, diethyl ether, and many gases easily solidify in liquid air. If, for example, carbon dioxide is passed through liquid air, it transforms into white flakes similar in appearance to snow. Mercury immersed in liquid air becomes solid and malleable.

Many substances cooled by liquid air sharply change their properties. For example, zinc and tin become so brittle that they readily transform into a powder, a lead bell emits a pure ringing sound, and a frozen rubber ball will be smashed to smithereens if it is dropped onto the floor.

Since the boiling point of oxygen (-183°C) is higher than that of nitrogen (-195.8°C), oxygen liquefies more easily than nitrogen. This is why liquid air is richer in oxygen than atmospheric air. In storage, liquid air becomes still richer in oxygen owing to the evaporation chiefly of nitrogen.

Liquid air is produced in large amounts. It is mainly used for obtaining oxygen, nitrogen, and noble gases from it. Separation is performed by rectification-fractional distillation.

10. Preparation and Properties of Oxygen

Oxygen was first obtained in the pure state by K. Scheele (Sweden) in 1772, and then in 1774 by J. Priestly (England), who separated it from mercury(II) oxide. Priestly did not know, however, that the gas he had obtained was contained in the air. Only several years later did A. Lavoisier, who studied the properties of this gas in detail, establish that it is a component of air.

Oxygen is produced in industry at present from air (see Sec. 9). In laboratories, commercially produced oxygen is used that is supplied in steel cylinders under a pressure of about 15 MPa. The most important laboratory method of its preparation is the electrolysis of

aqueous solutions of alkalis. Small amounts of oxygen can also be prepared by reacting a solution of potassium permanganate with an acidified solution of hydrogen peroxide (see p. 17), or by the thermal decomposition of certain oxygen-containing substances, for instance potassium permanganate:



Oxygen is a colourless odourless gas. It is somewhat heavier than air—the mass of one litre of oxygen in standard conditions is 1.43 g, and of one litre of air, 1.293 g. Oxygen dissolves sparingly in water: 100 volumes of water at 0 °C dissolve 4.9, and at 20 °C—3.1 volumes of oxygen.

Oxygen forms diatomic molecules characterized by a high stability: the standard enthalpy of atomization of oxygen is 498 kJ/mol. At room temperature, its dissociation into atoms is negligible and becomes noticeable only at 1500 °C.

We have already mentioned (see Vol. 1, p. 148) that the magnetic properties of oxygen point to the presence in the O_2 molecule of two unpaired electrons. The latter occupy the antibonding molecular π orbitals (Fig. 52 in Vol. 1, p. 156). The paramagnetic properties of oxygen manifest themselves, particularly, in that liquid oxygen is attracted by a magnet.

Oxygen forms compounds with all the chemical elements except for helium, neon, and argon. It reacts directly with most elements (exceptions are the halogens, gold, and platinum). The rate of reaction of oxygen with both elementary substances and compounds depends on the nature of the substance and its temperature. Some substances, for example, nitrogen monoxide or the hemoglobin of the blood, even at room temperature combine with the oxygen of the air at a considerable rate. Many oxidation reactions are accelerated by catalysts. For instance, a mixture of hydrogen and oxygen ignites at room temperature in the presence of dispersed platinum. A feature of many reactions of combination with oxygen is the evolution of heat and light. This process is known as **combustion**.

Combustion occurs much more vigorously in pure oxygen than in air. Although the same amount of heat is liberated here as in combustion in air, the process occurs more rapidly, and the heat evolved is not spent on heating the nitrogen of the air. This is why the temperature of combustion in oxygen is considerably higher than in air.

Oxygen plays an exceedingly important role in nature. It participates in one of the most important vital processes—respiration. Of great significance is another process which oxygen participates in—the decomposition and decay of dead animals and plants. Here complex organic substances transform into simpler ones (in the long run into CO_2 , water and nitrogen), and the latter again return to the general cycle of substances in nature.

Oxygen has many applications. It is used to intensify chemical reactions in many production processes (for example, in the production of sulphuric and nitric acids and in the blast furnace process). Oxygen is employed to obtain high temperatures. For this purpose, various combustible gases (hydrogen, acetylene) are burned in special burners. Oxygen is also used in medicine when respiration is difficult.

Mixtures of liquid oxygen with pulverized coal, wood flour, or with other combustible substances are called **oxyliquids**. They are very explosive and are used in blasting jobs.

11. Ozone

When electric sparks are passed through oxygen or air, a characteristic odour appears caused by the formation of a new substance—**ozone**. It can be prepared from absolutely pure dry oxygen. Hence it follows that ozone consists only of oxygen and is an allotropic modification of it.

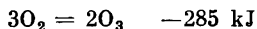
The molecular mass of ozone is 48. The atomic mass of oxygen is 16*. Consequently, an ozone molecule consists of three oxygen atoms.

Ozone is prepared by acting on oxygen with silent electric discharges. Devices used for this purpose are known as **ozonizers**.

In ordinary conditions, ozone is a gas. It can be separated from oxygen by deep cooling; ozone condenses to form a blue liquid boiling at -111.9°C .

The solubility of ozone in water is much greater than that of oxygen: 100 volumes of water at 0°C dissolve 49 volumes of ozone.

The formation of ozone from oxygen can be expressed by the equation



from which it follows that the standard enthalpy of formation of ozone is positive and is 142.5 kJ/mol . In addition, as the coefficients of the equation show, in the course of this reaction three molecules of a gas transform into two, i.e. the entropy of the system diminishes. As a result, the standard change in the Gibbs energy in this reaction is also positive (163 kJ/mol). Thus, the reaction of transformation of oxygen into ozone cannot proceed spontaneously—it requires the expenditure of energy. The reverse reaction—the decomposition of

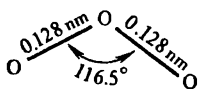


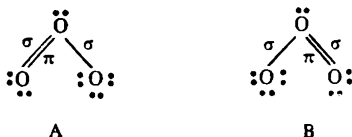
Fig. 6. Structure of an ozone molecule

* More precisely, 47.9982 and 15.9994, respectively.

ozone—proceeds spontaneously because it is attended by a decrease in the Gibbs energy of the system. In other words, ozone is an unstable substance.

The ozone molecule has the shape of an isosceles triangle. Its structure is shown schematically in Fig. 6. The angle at the vertex of the triangle is close to 120 degrees, which indicates that the central oxygen atom is in the state of sp^2 hybridization here. Accordingly, from the standpoints of the valence bond method, the formation of the O_3 molecule can be described as follows.

The hybrid sp^2 orbital of the central atom containing one electron (Fig. 7, left part) overlaps with the p_x orbital of one of the extreme oxygen atoms, the result being the formation of a sigma bond. The p_z orbital of the central atom not participating in the hybridization is oriented at right angles to the plane of the molecule and also contains an unpaired electron. It overlaps with the similarly arranged p_z orbital of the same extreme atom of oxygen, which leads to the formation of a pi bond. Finally, playing the role of the donor of the electron pair occupying one of the hybrid sp^2 orbitals (Fig. 7, right part), the central oxygen atom forms a sigma bond with the other extreme oxygen atom in the donor-acceptor way. Electron dot formula A



in which the dots stand for the unshared pair of electrons, and the sigma and pi bonds are indicated by the relevant Greek letters, corresponds to the structure formed.

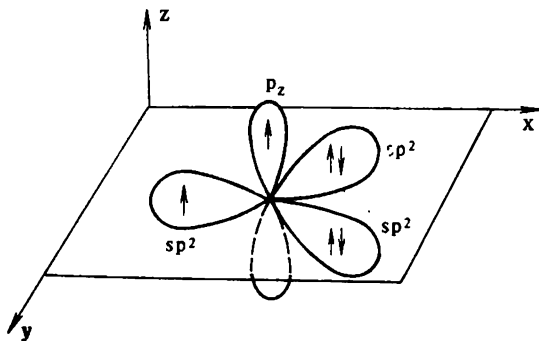


Fig. 7. Diagram of the orbitals of the central oxygen atom in an ozone molecule

According to formula *A*, the bonds of the central oxygen atom with the two extreme atoms are not equivalent—one is double, and the other is single. The identical length of these bonds, however (Fig. 6), points to their equivalence. Hence, in addition to formula *A*, the structure of the ozone molecule can with equal right be described by formula *B*. From the standpoints of the method of superposition of electron dot formulas (see Vol. 1, Sec. 44), this signifies that the formula of the ozone molecule is intermediate between *A* and *B* and can be written in the form:

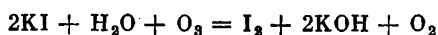


Here, the dashed lines indicate the delocalization of the pi electron pair, i.e. its belonging to all three oxygen atoms. Consequently, the pi bond in the ozone molecule is a three-centre one.

A consideration of the structure of the ozone molecule from the angle of view of the MO method also leads to the conclusion that a three-centre bonding molecular pi orbital is formed here.

Ozone is one of the strongest oxidizing agents. It oxidizes all metals except for gold and the platinum metals, and also most non-metals. It transforms lower oxides into higher ones, and metal sulphides into sulphates. In the course of the majority of these reactions, the ozone molecule loses one oxygen atom and transforms into the oxygen molecule O_2 .

Ozone liberates iodine from a solution of potassium iodide:



If we place a piece of paper wetted with solutions of KI and starch into air containing ozone, it immediately becomes blue. This reaction is used for detecting ozone.

Being a strong oxidizing agent, ozone kills bacteria and is therefore used for disinfecting water and air.

Ozone is poisonous. Its maximum allowable content in air is $10^{-5}\%$. Its odour is well discerned at this concentration. The ozone content in the layer of the atmosphere adjoining the Earth usually ranges from 10^{-7} to $10^{-60}\%$. It is formed in the atmosphere by electric discharges.

SULPHUR, SELENIUM, TELLURIUM

12. Occurrence and Preparation of Sulphur

Sulphur (*Sulfur*) occurs in nature in the free state (native sulphur) and in various compounds. Native sulphur deposits occur in the Soviet Union in the Kara-Kum desert in Turkmenia, in the Uzbek

SSR, and along the banks of the Volga River. The largest sulphur deposits in other countries are in the USA, Italy, and Japan.

Compounds of sulphur with various metals are very abundant. Many of them are valuable ores (for example, lead glance PbS , zinc blende ZnS , and copper glance Cu_2S) used to produce non-ferrous metals.

Among sulphur compounds, sulphates, chiefly of calcium and magnesium, are also quite abundant in nature. Finally, sulphur compounds are contained in the organisms of plants and animals.

The total sulphur content in the Earth's crust is about 0.1%.

Native sulphur contains impurities. They are separated by taking advantage of the low melting point of sulphur. But the sulphur produced by melting from its ore (brimstone) generally still contains many impurities. It is further purified by distillation in refining furnaces where the sulphur is heated to boiling. The sulphur vapour is fed into a brick-lined chamber. At first, while the chamber is cold, the sulphur directly solidifies and is deposited on the walls as a light-yellow powder (**flowers of sulphur**). When the chamber gets heated to above 120°C , the vapour condenses into a liquid that is tapped from the chamber into moulds, where it solidifies into rods. This is how **rod sulphur** is produced.

Iron pyrites FeS_2 , also known as **pyrite**, and polymetallic ores containing sulphur compounds of copper, zinc, and other non-ferrous metals are an important source of sulphur. A certain amount of sulphur (gas sulphur) is prepared from the gases formed in the coking and gasification of coal.

13. Properties and Uses of Sulphur

At ordinary pressures, sulphur forms brittle yellow crystals melting at 112.8°C ; its density is 2.07 g/cm^3 . It does not dissolve in water, but does dissolve quite well in carbon disulphide, benzene, and some other liquids. When these solvents are evaporated, sulphur

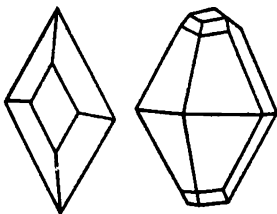


Fig. 8. Crystals of rhombic sulphur



Fig. 9. A crystal of monoclinic sulphur

separates from the solution in the form of transparent yellow crystals of the rhombic system having the shape of octahedra in which part of the corners or edges are usually cut off, as it were (Fig. 8). This modification of sulphur is called **rhombic**.

Crystals having a different shape are obtained if molten sulphur is slowly cooled and, when it has partly solidified, the remaining liquid that has not managed to solidify is poured off. In these conditions, the walls of the vessel will be coated inside with long dark yellow needle-shaped crystals of the monoclinic system (Fig. 9). This modification of sulphur is called **monoclinic**. It has a density of 1.96 g/cm^3 , melts at 119.3°C , and is stable only at a temperature above 96°C . At a lower temperature, the crystals of monoclinic sulphur become lighter in colour and transform into octahedra of rhombic sulphur.

Determination of the molecular mass of sulphur according to the depression of the freezing point of its solutions in benzene led to the conclusion that sulphur molecules consist of eight atoms (S_8). The same kind of molecules S_8 having a cyclic structure form crystals of rhombic and monoclinic sulphur. Thus, the difference between the properties of the crystalline modifications of sulphur is due not to a different number of atoms in the molecules (as, for instance, in oxygen and ozone molecules), but to the different structure of the crystals.

Of interest are the changes which sulphur undergoes if it is slowly heated to its boiling point. At 112.8°C , it melts and transforms into a yellow mobile liquid. Upon further heating, the liquid darkens and acquires a reddish-brown colour. At about 250°C , it becomes so thick that it does not pour out from the inverted vessel. Above 300°C , the liquid sulphur again becomes mobile, but its colour remains dark. Finally, at 444.6°C , sulphur boils, forming an orange-yellow vapour. In cooling, the same phenomena occur in the reverse sequence.

These changes are explained as follows. At temperatures exceeding $150\text{--}160^\circ\text{C}$, the cyclic S_8 molecules begin to break up. The chains of atoms that form combine with one another to make long chains owing to which the viscosity of the molten sulphur greatly increases. Further heating results in breaking up of these chains, and the viscosity of the sulphur diminishes again.

If molten sulphur heated to boiling is poured in a thin stream into cold water, it transforms into a soft rubbery brown mass that can be stretched out into filaments. This modification is known as **plastic sulphur**. The latter already in a few hours becomes brittle, acquires a yellow colour, and gradually transforms into the rhombic modification.

The number of atoms in a molecule of sulphur vapour gradually diminishes with elevation of the temperature: $\text{S}_8 \rightarrow \text{S}_6 \rightarrow \text{S}_4 \rightarrow$

→ $S_2 \rightarrow S$. At from 800 to 1400 °C, sulphur vapour consists mainly of diatomic molecules, at 1700 °C of atoms.

Sulphur is a typical non-metal. It combines directly with many metals such as copper, iron, and zinc with the evolution of a great amount of heat. It also combines with almost all non-metals, but not so readily and vigorously as with metals.

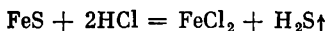
Sulphur is widely used in the national economy. It is employed in the rubber industry to cure crude rubber. The latter acquires its valuable properties only after being mixed with sulphur and heated to a definite temperature. This process is called **vulcanization** of rubber (p. 173). Rubber having a very large sulphur content is known as **ebonite**, it is a good electrical insulator.

Flowers of sulphur are used to combat certain plant pests. Sulphur is also employed for the production of matches, ultramarine (a blue pigment), carbon disulphide, and a number of other substances. In countries having rich sulphur deposits, it is used as the starting material in sulphuric acid production.

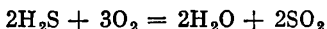
14. Hydrogen Sulphide. Sulphides

At a high temperature, sulphur combines with hydrogen to form the gas hydrogen sulphide.

Hydrogen sulphide is generally prepared in practice by reacting dilute acids with metal sulphides, for example with iron(II) sulphide:



Hydrogen sulphide is a colourless gas with the characteristic odour of rotten eggs. It is slightly heavier than air, liquefies at $-60.3^\circ C$, and solidifies at $-85.6^\circ C$. It burns in air with a bluish flame and forms sulphur dioxide and water:



If we introduce an object such as a porcelain cup into a hydrogen sulphide flame, the temperature of the latter will lower appreciably, and the hydrogen sulphide will be oxidized only to free sulphur that forms a yellow deposit on the cup:

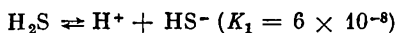


Hydrogen sulphide readily ignites; a mixture of it with air explodes. *Hydrogen sulphide is a strong poison.* The prolonged inhalation of air containing even small amounts of this gas causes serious poisoning.

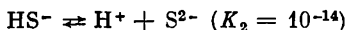
At $20^\circ C$, one volume of water dissolves 2.5 volumes of hydrogen sulphide. A solution of the latter in water is known as **hydrogen sulphide water**. When left standing in the air, especially in the light, hydrogen sulphide water soon becomes turbid because of the sulphur

separated. This occurs as a result of oxidation of the hydrogen sulphide by the oxygen of the air (see the preceding reaction). A solution of hydrogen sulphide in water has the properties of an acid.

Hydrogen sulphide is a weak dibasic acid. It dissociates in steps, the first step being the major one:

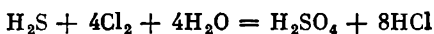


Further dissociation (the second step)



occurs to a negligibly small extent.

Hydrogen sulphide is a strong reducing agent. When acted upon by strong oxidizing agents, it oxidizes to sulphur dioxide or to sulphuric acid; the depth of oxidation depends on the conditions: the temperature, pH of the solution, and the concentration of the oxidizing agent. For instance, the reaction with chlorine customarily proceeds up to the formation of sulphuric acid:

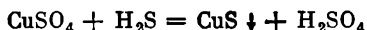


Hydrogen sulphide is encountered in nature in volcanic gases and in the water of mineral springs. It also forms in the decay of proteins in dead animals and plants and in the rotting of garbage.

The normal salts of hydrogen sulphide are called **sulphides**. They can be obtained in different ways, one of which is the direct contacting of the relevant metals with sulphur. If we mix, for instance, iron filings with powdered sulphur and heat the mixture at one spot, we can easily induce a reaction of the iron and the sulphur, which further proceeds spontaneously and is attended by the release of a large amount of heat:



Many sulphides can be prepared by acting with hydrogen sulphide on aqueous solutions of the salts of the relevant metals. For example, if hydrogen sulphide is passed through a solution of a copper(II) salt, a black precipitate of copper(II) sulphide appears:



The net ionic equation is



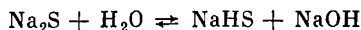
Although an acid is produced in the course of the reaction, the CuS precipitates: copper(II) sulphide dissolves neither in water nor in dilute acids. But no precipitate is obtained when hydrogen sulphide acts on a solution of an iron(II) salt—iron(II) sulphide FeS

is insoluble in water, but dissolves in acids. This difference is explained by the solubility product of CuS being much smaller than that of FeS (see Table 16 in Vol. 1, p. 263). The reaction of metal sulphides with acids is treated in greater detail in Vol. 1, p. 268.

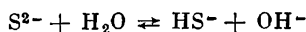
Some sulphides such as Na_2S and K_2S are soluble in water. It is obvious that they cannot be obtained from salts of the relevant metals by acting with hydrogen sulphide or other sulphides on them.

The difference in the solubility of sulphides is taken advantage of in analytical chemistry for the consecutive precipitation of metals from solutions of their salts.

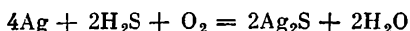
Sulphides are salts of a very weak acid and therefore readily hydrolyze. For example, Na_2S when dissolved in water hydrolyzes almost completely with the formation of the acid salt—sodium hydrogen sulphide:



or



Silver and copper objects blacken in air and in water containing hydrogen sulphide. This occurs because they become coated with a film of the corresponding sulphide. The oxidizing agent here is the oxygen contained in the air or dissolved in the water:



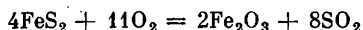
If a solution of a sulphide such as sodium sulphide is agitated with sulphur, the latter dissolves in it, and the residue after evaporation in addition to the sodium sulphide contains compounds with a greater sulphur content—from Na_2S_2 to Na_2S_5 . Such compounds are called **polysulphides**.

The sulphides include many compounds having a varying composition. For instance, iron(II) sulphide can have a composition ranging from $\text{FeS}_{1.01}$ to $\text{FeS}_{1.14}$.

Natural sulphides are the basic part of ores of non-ferrous and rare metals and are widely used in metallurgy. Some of them are also employed as the starting material for the production of sulphuric acid. A natural polysulphide—iron pyrite FeS_2 (see Secs. 12 and 15) is also used for the same purpose. Sulphides of alkali and alkaline-earth metals are used in the chemical and light industries. For example, Na_2S , CaS , and BaS are used in the leather industry for removing the hair from hides. Sulphides of alkaline-earth metals, zinc, and cadmium are the basis of luminophors (see p. 294). Some sulphides have semiconductor properties and are employed in electronics.

15. Sulphur Dioxide. Sulphurous Acid

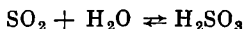
Sulphur dioxide SO_2 is formed when sulphur is burned in air or oxygen. It is also obtained by the calcination ("roasting") of metal sulphides in air. An example is iron pyrite:



This reaction is generally used to produce sulphur dioxide in industry (for other industrial methods of producing SO_2 see p. 59).

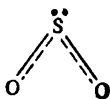
Sulphur dioxide is a colourless gas ("sulphurous gas") with the pungent odour of burning sulphur. It readily condenses into a colourless liquid boiling at -10.0°C . Evaporation of liquid SO_2 is attended by a sharp drop in the temperature (down to -50°C).

Sulphur dioxide is well soluble in water (about 40 volumes in one volume of water at 20°C); it reacts partly with the water to form sulphurous acid:



Thus, sulphur dioxide is the anhydride of sulphurous acid. Elevation of the temperature diminishes the solubility of SO_2 , and equilibrium shifts to the left, gradually all of the sulphur dioxide again separates from the solution.

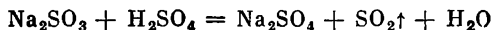
The SO_2 molecule is constructed similar to the ozone molecule. The nuclei of the atoms forming it compose an isosceles triangle:



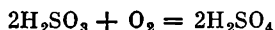
Here the sulphur atom, like the central oxygen atom in the ozone molecule, is in the sp^2 hybridized state, and the angle OSO is close to 120 degrees. The p_z orbital of the sulphur atom oriented at right angles to the plane of the molecule does not participate in hybridization. A three-centre pi bond is formed at the expense of this orbital and the similarly oriented p_z orbitals of the oxygen atoms; the pair of electrons forming it belongs to all three atoms of the molecule.

Sulphur dioxide is used for the production of sulphuric acid, and also (in considerably smaller quantities) for bleaching straw, wool, and silk, and as a disinfectant (for destroying mould fungi in basements, cellars, wine barrels, fermentation tanks, etc.).

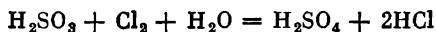
Sulphurous acid H_2SO_3 is very unstable. It is known only as aqueous solutions. When an attempt is made to recover sulphurous acid, it decomposes into SO_2 and water. For example, when concentrated sulphuric acid is used to act on sodium sulphite, sulphur dioxide is liberated instead of sulphurous acid:



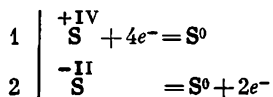
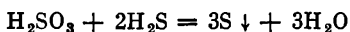
A solution of sulphurous acid must be protected from contact with the air because otherwise it absorbs oxygen from the air and slowly oxidizes into sulphuric acid:



Sulphurous acid is an excellent reducing agent. For example, it reduces free halogens to hydrogen halides:



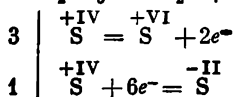
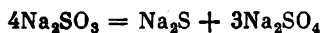
When reacting with strong reducing agents, however, sulphurous acid can play the role of an oxidizing agent. For instance, its reaction with hydrogen sulphide mainly follows the equation:



Sulphurous acid is dibasic ($K_1 \approx 2 \times 10^{-2}$, $K_2 = 6.3 \times 10^{-8}$) and forms two series of salts. Its normal salts are called **sulphites**, and the acid ones **hydrogen sulphites** (or acid sulphites)*.

Like the acid, sulphites and hydrogen sulphites are reducing agents. Their oxidation yields salts of sulphuric acid.

The sulphites of the most active metals when calcined decompose with the formation of sulphides and sulphates (a reaction of disproportionation):



Potassium and sodium sulphites are employed for bleaching some materials, in the textile industry in the dyeing of fabrics, and in photography. A solution of $\text{Ca}(\text{HSO}_3)_2$ (this salt exists only in solution) is used to process wood into sulphite pulp, from which paper is then made.

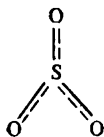
16. Sulphur Trioxide. Sulphuric Acid

Sulphur dioxide can attach oxygen, transforming into **sulphur trioxide**. In ordinary conditions, this reaction proceeds exceedingly slowly. It proceeds much more rapidly and easily at an elevated temperature and in the presence of catalysts.

* Sodium dithionate $\text{Na}_2\text{S}_2\text{O}_4$ —the sodium salt of dithionic acid $\text{H}_2\text{S}_2\text{O}_4$ —is sometimes erroneously named sodium hydrogen sulphite.

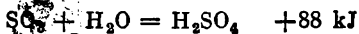
Sulphur trioxide is a colourless highly mobile liquid with a density of 1.92 g/cm^3 . It boils at 44.7°C and freezes at 16.8°C . In storage, especially in the presence of traces of moisture, this substance changes, transforming into long silky crystals.

Free molecules of SO_3 (in the gaseous state) are constructed in the form of an equilateral triangle with the sulphur atom at its centre and the oxygen atoms at its corners. As in the SO_2 molecule, the sulphur atom is in the sp^2 hybridized state here; accordingly, the nuclei of all four atoms in the SO_3 molecule are in one plane, and the valence angles OSO equal 120° degrees:

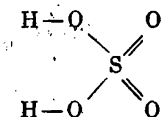


The sulphur atom in the SO_3 molecule is bonded to the oxygen atoms by three two-centre sigma bonds and one four-centre pi bond (compare with the structure of the SO_2 molecule—Sec. 15). Besides this, the formation of additional covalent bonds as in the Cl_2 molecule (p. 21) is possible at the expense of the unshared $2p$ electron pairs of the oxygen atoms and the free $3d$ orbitals of the sulphur atom.

Sulphur trioxide is the anhydride of sulphuric acid; the latter is formed when SO_3 reacts with water:



The structure of sulphuric acid molecules corresponds to the formula



Anhydrous H_2SO_4 is a colourless oily liquid freezing at 10.3°C .

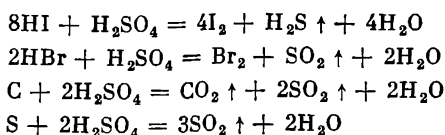
When anhydrous sulphuric acid ("monohydrate") is heated, it liberates SO_3 that volatilizes. This proceeds until an azeotropic solution is obtained containing 98.3% (mass) of H_2SO_4 and 1.7% (mass) of water. The solution boils and is distilled without any change in its composition at 338.8°C . An azeotropic solution is also obtained in the long run when dilute sulphuric acid is distilled. In this case, water is mainly distilled off until the concentration of the acid reaches 98.3% (mass).

The dissolution of sulphuric acid in water is attended by the formation of hydrates and the evolution of a very great amount

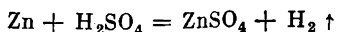
of heat. For this reason, care must be taken when mixing concentrated sulphuric acid with water. To avoid splashing out of the heated surface layer of the solution, it is necessary to pour the sulphuric acid (as the heavier substance) into the water in small portions or in a thin stream; water must never be poured into the acid.

Sulphuric acid avidly absorbs water vapour and is therefore often used for drying gases. Its ability to absorb water also explains why many organic substances, especially carbohydrates (cellulose, sugar, etc.) become charred when acted upon by concentrated sulphuric acid. Carbohydrates contain hydrogen and oxygen in the same ratio as water does. Sulphuric acid takes away from the carbohydrates hydrogen and oxygen that form water, while the carbon separates in the form of charcoal.

Concentrated sulphuric acid, especially when hot, is a vigorous oxidizing agent. It oxidizes HI and HBr (but not HCl) to the free halogens, carbon to CO_2 , and sulphur to SO_2 . These reactions can be expressed by the equations:

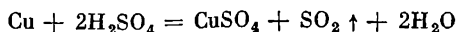


Sulphuric acid reacts differently with metals depending on its concentration. Dilute sulphuric acid oxidizes metals with its hydrogen ion. It therefore reacts only with the metals that precede hydrogen in the electromotive series, for example:

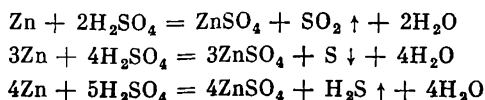


Lead, however, does not dissolve in the dilute acid because the salt PbSO_4 formed is insoluble.

Concentrated sulphuric acid is an oxidizing agent at the expense of sulphur(VI). It oxidizes all metals in the electromotive series up to silver inclusively. Its reduction products may vary depending on the activity of the metal and on the conditions (concentration of the acid, temperature). When it reacts with metals having a low activity, for instance with copper, the acid is reduced to SO_2 :

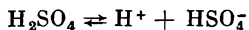


When it reacts with more active metals, the reduction products may be either SO_2 , free sulphur, or hydrogen sulphide. For example, the following reactions are possible with zinc:

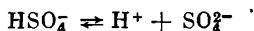


For the action of sulphuric acid on iron, see Sec. 128.

Sulphuric acid is a strong dibasic acid. In the first step in solutions with a moderate concentration, it dissociates virtually completely:



Dissociation in the second step

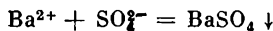


proceeds to a smaller degree. The dissociation constant of sulphuric acid in the second step, expressed through the activity of the ions, is $K_2 = 10^{-2}$.

Being a dibasic acid, sulphuric acid forms two series of salts—normal and acid ones. The normal salts are called **sulphates**, and the acid ones **hydrogen sulphates** (their previous name was bisulphates).

Most salts of sulphuric acid are quite well soluble in water. The sulphates of barium BaSO_4 , strontium SrSO_4 , and of lead PbSO_4 are practically insoluble. Calcium sulphate CaSO_4 dissolves only slightly. The solubility product of BaSO_4 is 1.1×10^{-10} , of SrSO_4 , 3.2×10^{-7} , of PbSO_4 , 1.6×10^{-8} , and of CaSO_4 , 1.3×10^{-4} .

Barium sulphate is insoluble not only in water, but also in dilute acids. Therefore, the formation of a white precipitate that is insoluble in acids when a barium salt is reacted with a solution indicates that the solution contains SO_4^{2-} ions:



Hence, soluble barium salts are reagents detecting the presence of the sulphate ion.

The most important salts of sulphuric acid include the following.

Sodium Sulphate Na_2SO_4 . It crystallizes from aqueous solutions with ten molecules of water ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). In this form it is called **Glauber's salt** after the German chemist and physician Johann Glauber who was the first to prepare it by reacting sulphuric acid with sodium chloride. The anhydrous salt is used in the manufacture of glass.

Potassium Sulphate K_2SO_4 . It consists of colourless crystals well soluble in water. It forms a number of double salts, including alums (see below).

Magnesium Sulphate MgSO_4 . It is contained in sea water. It crystallizes from solutions in the form of the hydrate $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

Calcium Sulphate CaSO_4 . It occurs in nature in large amounts as the mineral **gypsum** $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. When heated to $150\text{--}170^\circ\text{C}$, gypsum loses three-fourths of the water of crystallization in it and transforms into **plaster of Paris** ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$). When mixed with water to form a dough, plaster of Paris sets quite rapidly, again transforming into $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Owing to this property, gypsum is used to fabricate casting moulds and replicas of various objects, and also

as a binder for plastering walls and ceilings. Bandages made with it are used in surgery to hold broken bones in place.

Anhydrous calcium sulphate is called **anhydrite**.

Vitriols. This name is commonly used to designate the sulphates of copper, iron, zinc, and some other metals containing the water of crystallization.

Blue vitriol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ forms blue crystals. It is used for the electroplating of metals with copper, for preparing certain mineral pigments, and also as the starting substance in the production of other copper compounds. In agriculture, a dilute solution of blue vitriol is used for spraying plants and treating grain seeds before sowing them in order to destroy the spores of harmful fungi.

For **green vitriol** $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ see p. 363.

Alums. When a solution of potassium sulphate K_2SO_4 is added to a solution of aluminium sulphate $\text{Al}_2(\text{SO}_4)_3$ and the liquid is allowed to crystallize, beautiful colourless crystals form having the composition $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ or $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. This compound is called ordinary or **potassium alum** and is a double salt of sulphuric acid and the metals potassium and aluminium (for the applications of potassium alum see p. 308).

Double salts exist only in the solid state. An aqueous solution of potassium alum contains the ions K^+ , Al^{3+} , and SO_4^{2-} .

Alums can contain trivalent metals such as iron and chromium instead of aluminium, and sodium or ammonium instead of potassium. An example is chrome (or potassium chrome) alum $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$.

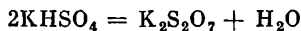
Disulphuric Acid. Oleum. A solution of sulphur trioxide in sulphuric acid is known as **oleum**. It is widely employed in industry, for instance for the purification of petroleum products, and for the production of certain dyes and explosives.

In oleum, part of the SO_3 molecules combine with sulphuric acid to form **disulphuric acid** $\text{H}_2\text{S}_2\text{O}_7$ (its obsolete name is pyrosulphuric acid):

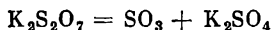


When oleum is cooled, disulphuric acid separates in the form of colourless crystals.

The salts of disulphuric acid—disulphates—are prepared by heating hydrogen sulphates. For example:



When heated to above their melting point, disulphates decompose with the liberation of SO_3 and transform into sulphates:



17. Production and Uses of Sulphuric Acid

Sulphuric acid is produced commercially by oxidizing sulphur dioxide SO_2 to the trioxide and then reacting the latter with water.

The sulphur dioxide needed for the production of the acid is obtained in a number of ways. The most widespread of them is the roasting of iron pyrite with the access of air (see p. 53).

In the USSR, preference is given, instead of iron pyrite, to **flotation pyrite**—a product obtained in the flotation (see p. 209) of copper ores having a low copper content, and to **coal pyrite** obtained in the concentration of coal having a high sulphur content.

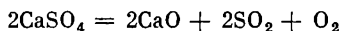
The iron(III) oxide formed in the roasting of iron pyrite ("burnt pyrites") is removed from the kilns and can be used for the production of iron, while the mixture of sulphur dioxide with the oxygen and nitrogen of the air is passed through purifying equipment where it is freed of dust and other impurities.

Sulphur dioxide is also produced by burning sulphur. In this case, a gas is formed that is free of harmful impurities. There is consequently no need to use purifying equipment, which considerably simplifies the production of sulphuric acid.

An important source of sulphur dioxide is the flue gases of non-ferrous metallurgical works. The significance of this source can be appreciated from the circumstance that in the production of one tonne of copper, 7.5 tonnes of SO_2 form, from which over 10 tonnes of sulphuric acid can be manufactured.

A large amount of SO_2 is extracted from flue gases obtained in the combustion of coal containing a lot of sulphur.

Other starting materials for the production of SO_2 are gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and anhydrite CaSO_4 . These minerals at 1350-1400 °C decompose to form SO_2 :



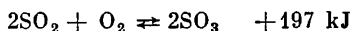
If gypsum mixed in the required proportion with iron(III) oxide Fe_2O_3 , aluminium oxide Al_2O_3 , and silica SiO_2 is calcined, cement is obtained in addition to sulphur dioxide.

Two processes are used to oxidize SO_2 in the production of sulphuric acid: the contact and the chamber ones.

In the **contact process**, oxygen combines with sulphur dioxide when these gases are brought into contact with a suitable catalyst. An indispensable condition for the success of the process is the complete removal of impurities from the reaction gases because even negligible traces of some substances (compounds of arsenic, phosphorus, etc.) "poison" the catalyst and cause it to rapidly lose its activity.

Vanadium pentoxide V_2O_5 is employed as the catalyst for oxidizing SO_2 .

In the production of sulphuric acid by the contact process, the mixture of sulphur dioxide and air after purification passes through a heater utilizing the gases coming out of the contact apparatus and enters the contact apparatus. Oxidation of the SO_2 to SO_3 takes place on the catalyst and is attended by the evolution of a considerable amount of heat:



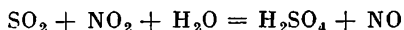
An increase in the oxygen content of the mixture increases the yield of SO_3 , shifting equilibrium to the right. At 450°C and excess oxygen in the mixture, the degree of conversion of SO_2 to SO_3 reaches 95 to 97%.

The sulphur trioxide formed in the contact apparatus is passed into 96-98% sulphuric acid, which becomes saturated with the SO_3 and transforms into oleum.

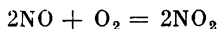
In Russia, sulphuric acid was first produced by the contact process at the Tentelev Plant (now the Krasny Khimik Plant) in Petersburg. The "Tentelev system" developed by chemists of this plant was one of the most progressive systems of its time and gained worldwide acknowledgement. Contact plants using this system were erected in a number of countries, including Japan and the USA.

The Chamber Process. The contact process of sulphuric acid production began to be used comparatively recently. Before this time, sulphuric acid was obtained exclusively by the chamber process, whose essence consists in oxidizing sulphur dioxide by nitrogen dioxide NO_2 in the presence of water.

Gaseous nitrogen dioxide reacts with sulphur dioxide as follows:



Upon giving up part of its oxygen to the sulphur dioxide, the NO_2 transforms into a different gas—nitrogen monoxide NO . The latter reacts with the oxygen of the air and again forms nitrogen dioxide:



that is used to oxidize new portions of SO_2 .

Hence, in the production of sulphuric acid, the NO is in essence a catalyst accelerating the process of oxidation of the sulphur dioxide.

The chemical industry produces several grades of sulphuric acid. They differ in their concentration, and also in their impurity content. The major part of the acid produced has a concentration of 91-94% and a density of 1.825-1.84 g/cm³.

Sulphuric acid is one of the most important products of the **fundamental chemical industry** which is responsible for the production of acids, alkalies, salts, mineral fertilizers, and chlorine. Sulphuric acid finds its main consumer in the manufacture of mineral fertiliz-

ers. It is also used for the production of many other acids, is employed in large amounts in organic synthesis, in the production of explosives, for refining kerosene, petroleum oils, and products of the coke-chemical industry (benzene, toluene), in the fabrication of paints, and in the pickling of ferrous metals (scale removal).

Before the October Socialist Revolution, the production of sulphuric acid in Russia was negligible in comparison with other countries. In 1913, all the plants produced a total of only 145 000 tonnes.

Matters changed sharply after the Revolution. The old plants were expanded and supplied with new equipment. A home base of raw materials was set up for the sulphuric acid industry and a number of new plants were erected. This made possible a considerable increase in sulphuric acid production:

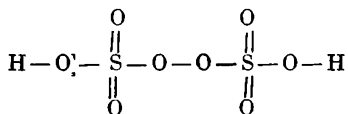
Year	1940	1964	1977
Production, thous. tonnes	1587	7647	21 100

18. Persulphuric Acid

In the electrolysis of a 50% solution of sulphuric acid, the hydrogen ions give up their charge at the cathode, and the HSO_4^- ions at the anode. After losing their charges, these ions combine in pairs to form persulphuric acid $\text{H}_2\text{S}_2\text{O}_8$:



Persulphuric acid is a derivative of hydrogen peroxide and an intermediate in the preparation of the latter by electrochemical means (see Sec. 3). Its structure can be expressed by the formula



As in hydrogen peroxide, two oxygen atoms are bonded here by a covalent bond forming the "chain" characteristic of peroxides. Such acids have been given the common name **peracids** and, in addition to sulphur, are known for a number of other elements. Much time was devoted to studying peracids by L. Pisarzhevsky*, to whom chemistry is under obligations for his classical investigations in this field.

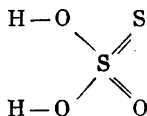
* Lev Vladimirovich Pisarzhevsky (1874-1938) was an outstanding scientist and teacher who boldly used the achievements of physics to study and explain chemical processes. His most important works are devoted to the studying of peroxides and peracids, the development of the theory of solutions, the application of the electronic theory to chemistry, and to development of the theory of galvanic cells.

All the peracids, like the peroxides, have strong oxidizing properties.

The salts of persulphuric acid—**persulphates**—are used for certain technical purposes, as a bleaching means, and as oxidizing agents in laboratory practice.

19. Thiosulphuric Acid

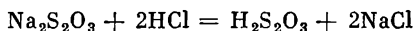
If we boil an aqueous solution of sodium sulphite Na_2SO_3 with sulphur and, after filtering off the excess sulphur, let the solution cool, colourless transparent crystals of a new substance separate from the solution whose composition is expressed by the formula $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. This substance is the sodium salt of thiosulphuric acid $\text{H}_2\text{S}_2\text{O}_3$.* The structural formula of thiosulphuric acid is as follows:



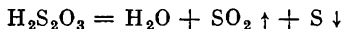
Thiosulphuric acid is unstable. It decomposes even at room temperature. Its salts—**thiosulphates**—are considerably more stable. The greatest use among them is found by sodium thiosulphate $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

When an acid, for instance hydrochloric acid, is added to a solution of sodium thiosulphate, the odour of sulphur dioxide appears, and after some time the liquid becomes turbid as a result of sulphur precipitating.

Apparently, first thiosulphuric acid is formed:

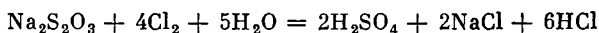


and it then decomposes according to the equation:



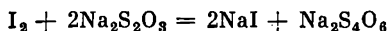
Investigation of the properties of sodium thiosulphate leads to the conclusion that the sulphur atoms in it are in different oxidation states: one of them has the oxidation number +4, and the other 0.

Sodium thiosulphate is a reducing agent. Chlorine, bromine, and other strong oxidizing agents oxidize it to sulphuric acid or to its salt. An example is:



* Substances that can be considered as being produced from oxygen-containing acids by the displacement of all or part of the oxygen in them by sulphur are called thioacids, and the salts corresponding to them—**thiosalts**. Particularly, thiosulphuric acid can be represented as sulphuric acid whose molecule contains a sulphur atom instead of one of the oxygen atoms. This is why it is customary practice to call $\text{H}_2\text{S}_2\text{O}_3$ "thiosulphuric acid".

The oxidation of sodium thiosulphate by weaker oxidizing agents proceeds differently. Iodine, for example, oxidizes sodium thiosulphate to the salt of **tetrathionic acid** $\text{H}_2\text{S}_4\text{O}_6$:



This reaction underlies one of the methods of quantitative chemical analysis (iodimetry) used to determine the content of certain oxidizing and reducing agents.

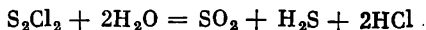
Tetrathionic acid $\text{H}_2\text{S}_4\text{O}_6$ belongs to the group of **polythionic acids**. The latter are dibasic acids of the general formula $\text{H}_2\text{S}_x\text{O}_6$, where x can take on values from 2 to 6, and possibly even higher ones. Polythionic acids are unstable and are known only in aqueous solutions. The salts of polythionic acids—**polythionates**—are more stable, some of them have been obtained as crystals.

Sodium thiosulphate is used in photography as a fixing salt (see p. 248), in the textile industry for the removal of the chlorine remaining after fabric bleaching, in medicine, and in veterinary.

20. Halogen Compounds of Sulphur

When chlorine is passed through molten sulphur, **sulphur(I) chloride** is formed that is a liquid boiling at 137°C . The molecular mass of this substance, as shown by the density of its vapour, corresponds to the formula S_2Cl_2 , and its name, accordingly, is **disulphur dichloride**.

Disulphur dichloride dissolves sulphur in an amount up to 66% (mass). Water decomposes S_2Cl_2 with the formation of sulphur dioxide, hydrogen chloride, and hydrogen sulphide:



Disulphide dichloride is used in the vulcanization of rubber.

Two other sulphur chlorides are known (SCl_2 and SCl_4) that have no practical significance. With fluorine, sulphur forms the gaseous sulphur hexachloride SF_6 , and with bromine it forms disulphur dibromide S_2Br_2 .

21. Selenium. Tellurium

Selenium is scarce in nature. Its content in the Earth's crust is 0.000 06% (mass). Its compounds occur in the form of impurities in the natural metal sulphides (PbS , FeS_2 , etc.). Hence, selenium is produced from the residues formed in the production of sulphuric acid, in the electrolytic refining of copper, and in some other processes.

Tellurium is one of the rare elements. Its content in the Earth's crust is only 0.000 001% (mass).

Selenium, like sulphur, forms several allotropic modifications in the free state, the most well known of which are **amorphous selenium**, a red-brown powder, and **gray selenium** that forms brittle crystals with a metallic lustre.

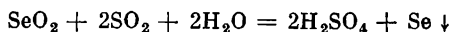
Tellurium is also known in the form of an amorphous modification and as light gray crystals with a metallic lustre.

Selenium is a typical semiconductor (see Sec. 76). Its especially important property as a semiconductor is the sharp increase in its electrical conductance when illuminated. A **barrier layer** is formed at the junction of selenium with a metallic conductor that can pass an electric current only in one direction. In view of this property, selenium is used in semiconductor engineering for the fabrication of rectifiers and photocells with a barrier layer. Tellurium is also a semiconductor, but its application is more restricted. The selenides and tellurides of some metals also have semiconductor properties and are employed in electronics. Tellurium is used in small amounts as an alloying addition to lead, improving its mechanical properties.

Hydrogen selenide H_2Se and hydrogen telluride H_2Te are colourless gases with a foul odour. Their aqueous solutions are acids whose dissociation constants are somewhat greater than that of hydrogen sulphide.

In their chemical properties, hydrogen selenide and hydrogen telluride exhibit an exceedingly great resemblance to hydrogen sulphide. Like the latter, they are strong reducing agents. They both decompose when heated. Hydrogen telluride is less stable than H_2Se : as in the hydrogen halide series, the stability of the molecules diminishes in the series $\text{H}_2\text{O} \rightarrow \text{H}_2\text{S} \rightarrow \text{H}_2\text{Se} \rightarrow \text{H}_2\text{Te}$. The salts of hydrogen selenide and hydrogen telluride—**selenides** and **tellurides**—are similar to sulphides as regards their solubility in water and acids. Hydrogen selenide and hydrogen telluride can be prepared by acting with strong acids on selenides and tellurides.

The dioxides SeO_2 and TeO_2 are obtained when selenium and tellurium are burned in air or in oxygen. They are solids in ordinary conditions and are the anhydrides of **selenous** H_2SeO_3 and **tellurous** H_2TeO_3 acids. Unlike sulphur dioxide, SeO_2 and TeO_2 exhibit mainly oxidizing properties and are readily reduced to free selenium and tellurium, for instance:



Strong acids can convert selenium and tellurium dioxides into selenic H_2SeO_4 and telluric H_2TeO_4 acids.

Selenic acid H_2SeO_4 is a strong acid. Like sulphuric acid, it has a low volatility, vigorously combines with water, chars organic substances, and has strong oxidizing properties. Its salts—**selenates**—are very similar to sulphates. The barium and lead salts of this acid, like their sulphate counterparts, are insoluble.

Telluric acid H_2TeO_4 , unlike selenic and sulphuric acids, is very weak. It separates from a solution as crystals of orthotelluric acid having the composition H_6TeO_6 . This is a hexabasic acid; it forms a number of salts, for instance silver orthotellurate Ag_6TeO_6 . When heated, orthotelluric acid detaches two water molecules and transforms into the dibasic acid H_2TeO_4 .

All selenium and tellurium compounds are poisonous.

4

THE MAIN SUBGROUP OF GROUP FIVE

The main subgroup of group five of the periodic table includes **nitrogen, phosphorus, arsenic, antimony, and bismuth.**

Since these elements have five electrons in the outer layer of an atom, they are characterized as a whole as non-metals. The ability to attach electrons, however, manifests itself considerably more weakly in them than in the corresponding elements of Groups VI and VII. Owing to the presence of five outer electrons, the maximum positive oxidation number of elements in this subgroup is +5, and the maximum negative one is -3. Because of the relatively lower electronegativity, the bond of the elements being considered with hydrogen is less polar than that with hydrogen of Group VI and VII elements. This is why the hydrogen compounds of these elements do not detach hydrogen ions in an aqueous solution and, consequently, have no acid properties.

Table 5
Selected Properties of Nitrogen and Its Analogues

	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Configuration of outer electron layer of atom	$2s^2 2p^3$	$3s^2 3p^3$	$4s^2 4p^3$	$5s^2 5p^3$	$6s^2 6p^3$
Ionization energy of atom, eV	14.53	10.49	9.82	8.64	7.3
Relative electronegativity	3.07	2.2	2.1	1.8	1.7
Atomic radius, nm	0.071	0.13	0.148	0.161	0.182
Melting point, °C	-210.0	44.1*	**	630.5	271.3
Boiling point, °C	-195.8	257	**	1634	1550
Density, g/cm ³	0.813*	1.83*	5.724*	6.68	9.80

* White phosphorus.

** Sublimes at 615 °C.

3* Liquid at -196 °C.

4* Gray arsenic.

The physical and chemical properties of the nitrogen subgroup elements change with an increasing atomic number in the same sequence that was observed in the groups already dealt with. But since the non-metallic properties of nitrogen are less pronounced than those of oxygen, and moreover than those of fluorine, the weakening of these properties when passing over to the following elements results in the appearance and increase in the metallic properties. The latter are perceptible already in arsenic, antimony has both kinds of properties to an approximately equal extent, and in bismuth the metallic properties predominate over the non-metallic ones.

The most important properties of the elements of the subgroup being considered are given in Table 5.

NITROGEN [NITROGENIUM] *

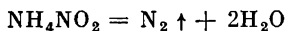
22. Occurrence of Nitrogen. Preparation and Properties

The major part of nature's nitrogen is in the free state. Free nitrogen is the main component of air, which contains 78.2% (vol.) of it. Inorganic nitrogen compounds are not encountered in nature in large amounts if we omit sodium nitrate NaNO_3 forming thick deposits along the Pacific coast of Chile. The soil contains insignificant amounts of nitrogen, mainly in the form of nitric acid salts. But all living organisms contain nitrogen as a constituent of the complex organic compounds called proteins. The transformations which proteins undergo in the cells of plants and animals form the foundation of all vital processes. **There is no life without protein**, and since protein must contain nitrogen, we can understand the important role played by this element in nature.

The total nitrogen content in the Earth's crust (including the hydrosphere and the atmosphere) is 0.04% (mass).

The preparation of nitrogen from the air mainly consists in its separation from oxygen. This is done in industry by evaporating liquid air in special installations.

Laboratories generally use nitrogen supplied in cylinders under an increased pressure or in Dewar flasks. Nitrogen can be prepared by the decomposition of certain of its compounds, for instance ammonium nitrite NH_4NO_2 , which is decomposed with the liberation of nitrogen when comparatively slightly heated:



In the nitrogen molecule N_2 , the atoms are bonded by a triple bond. The dissociation energy of this molecule is very high (946 kJ/mol),

* The Latin name *nitrogenium* literally means "giving birth to nitre".

consequently thermal dissociation of nitrogen becomes appreciable only upon very strong heating (about 0.1% dissociates at 3000 °C).

Nitrogen is a colourless gas having no odour and very poorly soluble in water. It is slightly lighter than air: the mass of one litre of nitrogen is 1.25 grams.

Molecular nitrogen is a substance with a low chemical activity. At room temperature, it reacts only with lithium. The low activity of nitrogen is explained by the high stability of its molecules that underlies the high activation energy of reactions proceeding with the participation of nitrogen. When heated, however, it begins to react with many metals—with magnesium, calcium, and titanium. Nitrogen reacts with hydrogen at a high temperature and pressure in the presence of a catalyst. Its reaction with oxygen begins at 3000-4000 °C.

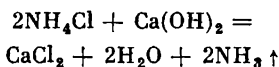
Animals placed in a nitrogen atmosphere quickly perish, not because of nitrogen poisoning, but owing to the absence of oxygen.

Nitrogen is mainly used as a reactant in the synthesis of ammonia and certain other compounds. It is also used for filling electric bulbs, for providing an inert medium in the industrial conducting of some chemical reactions, and in the pumping of combustible liquids.

23. Ammonia and Its Salts

Nitrogen forms several compounds with hydrogen. The most important of them is ammonia—a colourless gas with a characteristic sharp odour (the odour of “smelling salts”).

Ammonia is usually prepared in the laboratory by heating ammonium chloride NH_4Cl with slaked lime $\text{Ca}(\text{OH})_2$. The following reaction occurs:



The liberated ammonia contains water vapour. It is passed for drying through soda lime (a mixture of lime and sodium hydroxide).

The mass of one litre of ammonia in standard conditions is 0.77 g. Since this gas is considerably lighter than air, it can be gathered in an inverted vessel.

When cooled to -33.4°C under atmospheric pressure, ammonia transforms into a transparent liquid. The latter freezes at -77.8°C .

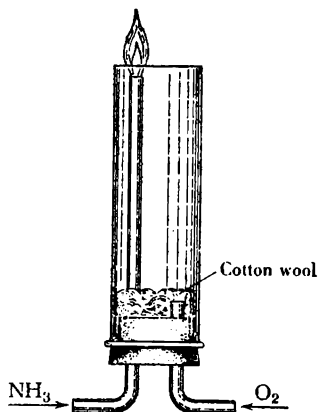


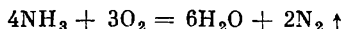
Fig. 10. Apparatus for showing how ammonia burns in oxygen

The electron configuration and spatial structure of the ammonia molecule were treated in Vol. 1, Sec. 43. In liquid ammonia, the NH_3 molecules ($\mu = 1.48 \text{ D}$) are bonded to one another by means of hydrogen bonds. This is the explanation of the comparatively high boiling point of ammonia (-33.4°C) which does not correspond to its low molecular mass (17 amu).

Ammonia dissolves very well in water: one volume of water at room temperature dissolves about 700 volumes of ammonia. A concentrated solution contains 25% (mass) of NH_3 and has a density of 0.91 g/cm^3 . An aqueous solution of ammonia in water is sometimes called **spirits** (or **spirit**) of **ammonia**. The conventional medicinal spirit of ammonia contains 10% of NH_3 . With elevation of the temperature, the solubility of ammonia diminishes. Consequently, it is liberated from a concentrated solution when heated. This is sometimes taken advantage of in laboratories to obtain small quantities of gaseous ammonia.

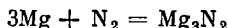
At a low temperature, the crystal hydrate $\text{NH}_3 \cdot \text{H}_2\text{O}$ melting at -79°C can be separated from an ammonia solution. A crystal hydrate of the composition $2\text{NH}_3 \cdot \text{H}_2\text{O}$ is known. The water and ammonia molecules in these hydrates are bonded to one another by means of hydrogen bonds.

Ammonia is quite active chemically. It reacts with many substances. Since nitrogen has its minimum oxidation number in ammonia (-3), the latter has only reducing properties. If ammonia is allowed to flow through a tube inserted into a wider tube (Fig. 10) through which oxygen is flowing, the ammonia can easily be ignited; it burns with a pale greenish flame. The combustion of ammonia yields water and free nitrogen:

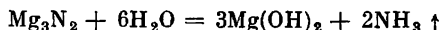


In other conditions, ammonia can be oxidized to nitrogen monoxide NO (see Sec. 29).

Unlike the hydrogen compounds of the non-metals of Groups VI and VII, ammonia has no acid properties. The hydrogen atoms in its molecule, however, can be displaced by metal atoms. When the hydrogen is completely displaced by a metal, a compound called a **nitride** is formed. Some nitrides, for instance those of calcium and magnesium, are obtained upon the direct reaction of nitrogen with the relevant metal at a high temperature:

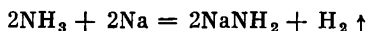


Many nitrides become completely hydrolyzed in water with the formation of ammonia and the metal hydroxide. An example is:

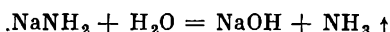


The compounds formed when only one hydrogen atom in ammonia molecules is displaced by a metal are known as **metal amides**. For

example, **sodium amide** (sodamide) is obtained as colourless crystals when ammonia is passed over molten sodium:

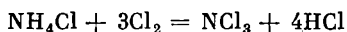


Water decomposes sodium amide:



Since sodium amide has strong basic and dehydrating properties, it is used in some organic syntheses, for example, in the production of the dye indigo and of certain medicinal preparations.

The hydrogen in ammonia can also be displaced by halogens. For instance, when chlorine acts on a concentrated solution of ammonium chloride, **nitrogen trichloride** NCl_3 is produced:

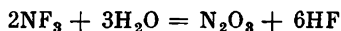
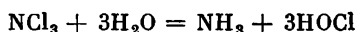


in the form of a heavy oily explosive liquid.

Nitrogen triiodide has similar properties. It forms as a black insoluble powder when iodine reacts with ammonia. It is harmless when moist, but the dried compound explodes at the least touch, liberating a purple iodine vapour.

With fluorine, nitrogen forms the stable compound **nitrogen trifluoride** NF_3 .

Inspection of Table 6 in Vol. 1 (p. 129) shows that the electronegativity of chlorine and iodine is less, and of fluorine is greater than that of nitrogen. It thus follows that in the compounds NCl_3 and NI_3 , the oxidation number of nitrogen is -3 , while in NF_3 it is $+3$. For this reason, nitrogen trifluoride differs in its properties from nitrogen trichloride and triiodide. For instance, the reaction of NCl_3 or NI_3 with water yields ammonia, whereas when NF_3 is reacted with water, the products include dinitrogen trioxide:

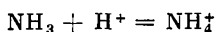


The nitrogen atom in the ammonia molecule is bonded with the aid of three covalent bonds to the hydrogen atoms, retaining one unshared electron pair:

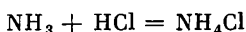


The nitrogen atom plays the role of an electron pair donor. It can participate in the formation of a fourth covalent bond with other atoms or ions having electron-acceptor properties according to the donor-acceptor method. This explains the ability of ammonia to enter into combination reactions, which is exceedingly characteristic of it.

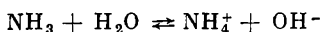
Examples of complex compounds formed by ammonia as a result of combination reactions are given in Secs. 86 and 87, and also in Chap. 8. In Vol. 1 (p. 136), we have already considered the reaction of the ammonia molecule NH_3 with a hydrogen ion leading to the formation of the ammonium ion NH_4^+ :



Ammonia is a proton acceptor in this reaction, and, consequently, from the standpoint of the proton theory of acids and bases (Vol. 1, p. 258), it exhibits basic properties. Indeed, reacting with acids that are in the free state or in a solution, ammonia neutralizes them and forms **ammonium salts**. For instance, its reaction with hydrogen chloride produces ammonium chloride NH_4Cl :



The reaction of ammonia with water also leads to the formation of not only ammonia hydrates, but also partly of the ammonium ion:



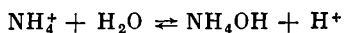
The result is an increase in the concentration of OH^- ions in the solution. This is exactly why aqueous solutions of ammonia have an alkaline reaction. According to an established tradition, however, the aqueous solution of ammonia is generally denoted by the formula NH_4OH and is called ammonium hydroxide, and the alkaline reaction of this solution is treated as the result of dissociation of the NH_4OH molecules.

Ammonia is a weak base. At 18°C , the equilibrium constant of its ionization (see the preceding equation) is 1.8×10^{-5} . One litre of a unimolar aqueous solution of ammonia contains only 0.0042 equivalent of the OH^- and NH_4^+ ions. Such a solution has a pH of 11.77 at 18°C .

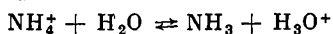
Most ammonium salts are colourless and well soluble in water. In some of their properties, they are similar to the salts of the alkali metals, especially of potassium (the K^+ and NH_4^+ ions are close in size).

Since an aqueous solution of ammonia is a weak base, ammonium salts become hydrolyzed in solutions. Solutions of salts formed by ammonia and strong acids have a weakly acid reaction.

The hydrolysis of the ammonium ion is usually written as:

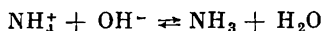


It is more proper, however, to consider it as a reversible transition of a proton from an ammonium ion to a water molecule:



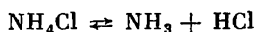
When an alkali is added to an aqueous solution of an ammonium salt, the ions H_3O^+ combine with the ions OH^- into water molecules,

and hydrolysis equilibrium shifts to the right. The process can be expressed by the equation



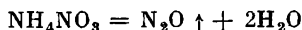
When the solution is heated, the ammonia volatilizes and can easily be detected by its odour. Hence, the presence of any ammonium salt in a solution can be detected by heating the latter with an alkali (an ammonium ion test).

Ammonium salts are thermally unstable. When heated, they decompose reversibly or irreversibly. Ammonium salts whose anion is not an oxidizing agent or exhibits oxidizing properties only to a small extent decompose reversibly. For example, ammonium chloride when heated appears to sublime—it decomposes into ammonia and hydrogen chloride, which again combine into ammonium chloride on the cold parts of the vessel:



In the reversible decomposition of ammonium salts formed by non-volatile acids, only ammonia volatilizes. The decomposition products—ammonia and the relevant acid—when mixed, however, again combine with each other. This can be exemplified by the reactions of decomposition of ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$ or ammonium phosphate $(\text{NH}_4)_3\text{PO}_4$.

Ammonium salts whose anion exhibits more sharply expressed oxidizing properties decompose irreversibly: a redox reaction proceeds in the course of which the ammonium ion is oxidized and the anion is reduced. Examples are the decomposition of NH_4NO_2 (Sec. 22) or of ammonium nitrate:



Ammonia and ammonium salts have found widespread application. We have already mentioned that ammonia even at a low pressure (0.7 to 0.8 MPa) readily transforms into a liquid. Since the evaporation of liquid ammonia is attended by the absorption of a great amount of heat (1.37 kJ/g), liquid ammonia is used in various refrigerating equipment.

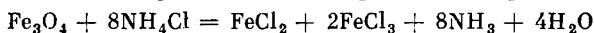
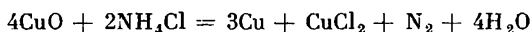
Aqueous solutions of ammonia are used in chemical laboratories and production processes as a weak volatile base. They are also employed in medicine and domestically. But the major part of the ammonia manufactured by the chemical industry goes to produce nitric acid and other nitrogen-containing substances. The most important of them include nitrogen fertilizers, primarily ammonium sulphate and nitrate, and carbamide (p. 112).

Ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$ is a good fertilizer and is produced in large amounts.

Ammonium nitrate NH_4NO_3 is also used as a fertilizer; the fraction of assimilated nitrogen in this salt is higher than in other ni-

trates or ammonium salts. Ammonium nitrate also forms explosive mixtures with combustible substances (**ammonals**) used for blasting jobs.

Ammonium chloride, or **sal ammoniac**, NH_4Cl is used in the dyeing industry, in textile printing, in soldering and tinning, and also in galvanic cells. Its use in soldering is based on the fact that it facilitates the removal of oxide films from the surface owing to which the solder adheres well to the metal. When the greatly heated metal comes into contact with ammonium chloride, the oxides on the metal surface are either reduced or converted into chlorides. The latter, being more volatile than the oxides, leave the metal surface. For copper and iron, the main processes occurring here are as follows:



The first of these reactions is a redox one: the copper, being a less active metal than the iron, is reduced by the ammonia formed when the NH_4Cl is heated.

Liquid ammonia and ammonium salts saturated with it are used as fertilizers. One of the main advantages of these fertilizers is their increased nitrogen content.

24. Fixation of Atmospheric Nitrogen.

Preparation of Ammonia

Up to the end of the nineteenth century, ammonia was produced commercially only as a by-product in the coking of coal. Coal contains from 1 to 2% of nitrogen. In the dry distillation of coal, virtually all of this nitrogen separates in the form of ammonia and ammonium salts. These two products are separated from the other gaseous products of dry distillation by passing the coke gas through water. Ammonia is liberated from this **ammonia** (or **gas**) **liquor** by heating it with lime.

Ammonia liquor was the only source of ammonia for a long time. But at the beginning of the twentieth century, new industrial methods of producing ammonia were developed that are based on the binding, or fixation, as chemists say, of atmospheric nitrogen. To assess the tremendous significance these discoveries had for mankind, we must get a clear idea of the role played by nitrogen in vital processes.

We have already mentioned that nitrogen is an essential constituent of proteins and is needed by every living being. Notwithstanding the enormous, virtually inexhaustible amount of free nitrogen in the atmosphere, neither animals nor plants (with a few exceptions) can use this nitrogen directly for nutrition.

Plants take nitrogen from the soil where it is chiefly contained as various organic compounds that gradually transform into salts of nitric acid and of ammonium. These salts dissolve in the soil water, are absorbed by the roots of plants, and are transformed into proteins in their cells.

Animals cannot assimilate nitrogen even in the form of salts. Their food must contain proteins produced by plants or by other animals. This is why the existence of animals depends completely on plants; only the latter provide them with the nitrogen they need.

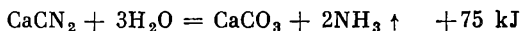
The soil generally contains very minute amounts of nitrogen which is constantly extracted from it by plants. When a crop is harvested, the nitrogen extracted by the plants from the soil is taken away with it. The soil is thus rapidly exhausted, and its fertility gradually diminishes. Hence, to obtain good crops, the nitrogen in the soil must constantly be replenished by introducing various nitrogen fertilizers into it.

Before World War I of 1914-1918, the chief mineral nitrogen fertilizer was the sodium nitrate (Chile saltpetre) imported to Europe from South America. It was also the only kind of starting substance for the preparation of nitric acid needed in the production of explosives and other nitrogen compounds. The limited supplies of natural saltpetre, their remoteness from the main consumers, and, primarily, the desire to do without the import of starting materials confronted the chemical industry of many countries with the task of using atmospheric nitrogen to produce nitrogen compounds. The successful coping with this task was one of the major achievements of chemistry at the beginning of the twentieth century. Several technical methods of binding atmospheric nitrogen were discovered during one decade.

The first to be discovered (1904) was the **cyanamide process** for producing ammonia. It is based on the ability of nitrogen to react with calcium carbide CaC_2 at a high temperature and form **calcium cyanamide*** CaCN_2 :



Calcium cyanamide is a powder coloured dark gray by an admixture of carbon. When reacted with steam at a pressure of about 0.6 MPa, it readily decomposes with the formation of ammonia and calcium carbonate:

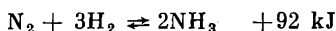


The first calcium cyanamide plant with an annual capacity of 4000 tonnes was erected in 1906 in Italy. In 1921, the world production of calcium cyanamide reached 500 000 tonnes a year. But after

* Calcium cyanamide $\text{Ca}=\text{N}-\text{C}\equiv\text{N}$ can be considered as a derivative of cyanamide $\text{H}_2\text{N}-\text{CN}$.

this, the building of new plants virtually stopped because another method for the commercial production of ammonia—the **synthesis of ammonia from hydrogen and nitrogen**—acquired paramount significance*.

At room temperature, nitrogen does not react with hydrogen. But it has been known for a long time that if electric sparks are passed through a mixture of these gases, a certain amount of ammonia is formed. Detailed investigation of this reaction showed that it is reversible:



At the high temperature produced by the electric discharges, equilibrium is shifted greatly to the left—the amount of ammonia produced is very small. For a long time, all attempts to increase this amount were unsuccessful. Only at the beginning of the twentieth century were the conditions finally found in which the yield of ammonia becomes sufficient for conducting the process in industrial conditions. It was found that these conditions are a high pressure and low temperature (see Vol. 1, Sec. 64).

But at low temperatures, the rate of the reaction is so slow that too much time would be needed to obtain considerable amounts of ammonia. Suitable catalysts were found to accelerate the process. Among the different substances studied, porous iron prepared in a definite way and containing small amounts of aluminium, potassium, calcium, and silicon oxides was found to be the best catalyst of the process.

The reaction is conducted at a temperature of about 500 °C, the resulting shift in equilibrium to the left being compensated by a higher pressure. Figure 11 shows how the ammonia content changes when equilibrium is reached in the system depending on the temperature and pressure. It can easily be seen that the same yield of ammonia can be obtained both at a comparatively low temperature and at a higher one if the pressure

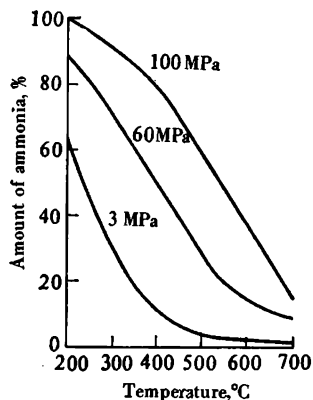
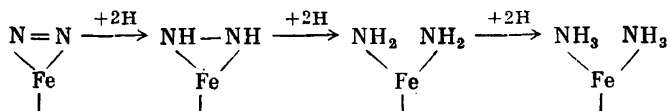


Fig. 11. Temperature dependence of ammonia yield at various pressures

* At present, the major part of the calcium cyanamide produced is used directly as a nitrogen fertilizer. Part of the calcium cyanamide is converted into carbamide (see p. 112) and cyanide compounds. It is also used as a defoliant, i.e. a substance causing plants to shed their leaves, which facilitates harvesting of a crop with the aid of machinery.

is raised in the latter case. But elevation of the temperature is attended by an increase in the reaction rate, and the required amount of ammonia is produced in a shorter time.

In synthesizing ammonia on an iron catalyst, the first step of the reaction is the adsorption of hydrogen and nitrogen molecules by the iron. The hydrogen molecules dissociate into atoms, while the nitrogen ones become less stable—part of the bonds in them become broken. Next the reaction approximately proceeds as follows:



The ammonia molecules formed on the surface of the catalyst are displaced by nitrogen molecules, and conversion is repeated.

All the industrial installations for ammonia synthesis follow the **circulation principle**: after the reaction the mixture of gases is cooled, the ammonia contained in it condenses and is separated, while the unreacted nitrogen and hydrogen are mixed with a fresh portion of gases, again fed onto the catalyst, and so on. The use of circulation increases the output of the entire system.

Ammonia can be synthesized at various pressures from 15 to 100 MPa. The greatest favour has been given to systems operating at a moderate pressure (30 MPa); they are most expedient from the economical viewpoint.

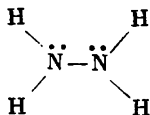
At present, the synthesis of ammonia is the basic method of binding atmospheric nitrogen.

25. Hydrazine. Hydroxylamine. Hydrazoic Acid

In addition to ammonia, nitrogen forms several other compounds with hydrogen, which are not so significant, however, as ammonia. The most important of them are described below.

Hydrazine N_2H_4 , a colourless liquid boiling at 113.5°C , is obtained by reacting sodium hypochlorite NaOCl with a concentrated solution of ammonia.

The structural formula of hydrazine is:

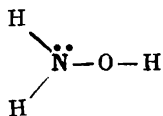


The nitrogen atoms in the hydrazine molecule have unshared pairs of electrons. This underlies the ability of hydrazine to enter into combination reactions. Hydrazine dissolves well in water; when it reacts with acids it attaches one or two hydrogen ions in the donor-

acceptor way, forming two series of salts. Examples are hydrazine hydrochloride $\text{N}_2\text{H}_4 \cdot \text{HCl}$ and hydrazine chloride $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$. Consequently, hydrazine has basic properties.

Hydrazine is a good reducing agent. When it burns in an atmosphere of air or oxygen, a very large amount of heat is evolved, and for this reason hydrazine has found use as a constituent part of the fuel of rocket engines. *Hydrazine and all its derivatives are strong poisons.*

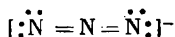
Hydroxylamine NH_2OH forms colourless crystals with a melting point of about 33°C . Its structural formula is:



In the hydroxylamine molecule, the nitrogen atom has an unshared pair of electrons. Consequently, like ammonia and hydrazine, it can enter into combination reactions to form donor-acceptor bonds. Hydroxylamine dissolves well in water, while with acids it produces salts, for instance hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$). The oxidation state of the nitrogen in hydroxylamine is -1 . This is why it exhibits both reducing and oxidizing properties. The reducing power of hydroxylamine, however, is greater. Particularly, it is used as a reducing agent (mainly in the form of its salts) in laboratory practice. It is also used in the production of some organic substances.

Hydrazoic acid HN_3 can be prepared by reacting nitrous acid HNO_2 with an aqueous solution of hydrazine. It is a colourless liquid with a pungent odour that boils at 36°C .

Hydrazoic acid is a weak acid ($K = 3 \times 10^{-5}$). In an aqueous solution, it dissociates into H^+ and N_3^- ions. The anion of hydrazoic acid N_3^- has a linear structure. Its electron dot formula is

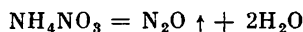


Both hydrazoic acid itself, and its salts—**azides**—are very explosive. Lead azide $\text{Pb}(\text{N}_3)_2$ is used to fill detonating fuses.

26. Oxides of Nitrogen

Nitrogen forms a number of oxides with oxygen. All of them can be prepared from nitric acid or its salts.

Dinitrogen oxide (nitrous oxide) N_2O is produced by heating ammonium nitrate:



Dinitrogen oxide is a colourless gas with a weak odour and a sweetish taste. It dissolves poorly in water: one volume of water at 20 °C dissolves 0.63 volume of N_2O .

Dinitrogen oxide is a thermodynamically unstable compound. The standard Gibbs energy of its formation is positive ($\Delta G_{\text{form}}^\circ = 104 \text{ kJ/mol}$). But owing to the high strength of the bonds in the N_2O molecule, the activation energies of reactions proceeding with the participation of this substance are high. Particularly, the energy of decomposition of N_2O is great. Therefore, dinitrogen oxide is stable at room temperature. At elevated temperatures, however, it decomposes into nitrogen and oxygen; the rate of decomposition grows with increasing temperature.

Dinitrogen oxide does not react with water, with acids, or with alkalis.

The electron structure of the N_2O molecule was treated in Vol. 1, Sec. 41.

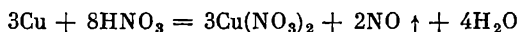
The inhalation of small amounts of dinitrogen oxide deadens the sensitivity to pain, which is why this gas is sometimes used in a mixture with oxygen as an anaesthetic. Large amounts of dinitrogen oxide excite the nervous system, and for this reason it was previously known as "laughing gas".

Nitrogen monoxide (or **nitrogen oxide**, or **nitric oxide**) is a colourless gas lending itself to liquefaction with difficulty. Liquid nitrogen monoxide boils at -151.7°C and freezes at -163.7°C . It dissolves poorly in water: one volume of water at 0°C dissolves only 0.07 volume of NO .

Nitrogen monoxide with respect to its chemical properties belongs among the indifferent oxides because it forms no acid.

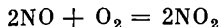
Like N_2O , nitrogen monoxide is thermodynamically unstable—the standard Gibbs energy of its formation is positive ($\Delta G_{\text{form}}^\circ = 86.6 \text{ kJ/mol}$). But, again like N_2O , at room temperature NO does not decompose because its molecules are sufficiently stable. Only at temperatures above 1000°C does its decomposition into nitrogen and oxygen begin to proceed at an appreciable rate. At very high temperatures, for reasons considered in Vol. 1, Sec. 65, the decomposition of NO does not proceed to completion—equilibrium sets in in the system $\text{NO}-\text{N}_2-\text{O}_2$. Because of this circumstance, nitrogen monoxide can be prepared from elementary substances at temperatures of an electric arc ($3000-4000^\circ\text{C}$).

Nitrogen monoxide is generally prepared in the laboratory by reacting 30-35% nitric acid with copper:

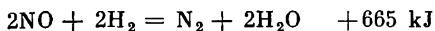


In industry, it is an intermediate in the production of nitric acid (see Sec. 29).

Nitrogen monoxide is characterized by oxidation-reduction duality. Strong oxidizing agents cause it to oxidize, while in the presence of strong reducing agents it becomes reduced. For example, it is readily oxidized by the oxygen of the air to nitrogen dioxide:



At the same time, a mixture of equal volumes of NO and H₂ explodes when heated:



The electron structure of the NO molecule can be described the best by means of the molecular orbital method. Figure 12 contains an energy-level diagram showing how the MO's are filled in the NO molecule (compare with similar diagrams for the N₂ and CO molecules—Vol. 1, Figs. 51 and 53 on pp. 156 and 157). The molecule NO has one electron more than the molecules N₂ and CO. This electron is in the antibonding orbital $\pi^{\text{ab}} 2p$. Hence, the number of bonding electrons here exceeds that of antibonding electrons by five. This corresponds to a bond multiplicity of 2.5 (i.e. $5:2 = 2.5$). Indeed, the energy of dissociation of the NO molecule into atoms (632 kJ/mol) has an intermediate value in comparison with the relevant values for the O₂ molecule (498 kJ/mol), in which the bond multiplicity is two, and the N₂ molecule (945 kJ/mol), in which the bond is triple. At the same time, as regards its dissociation

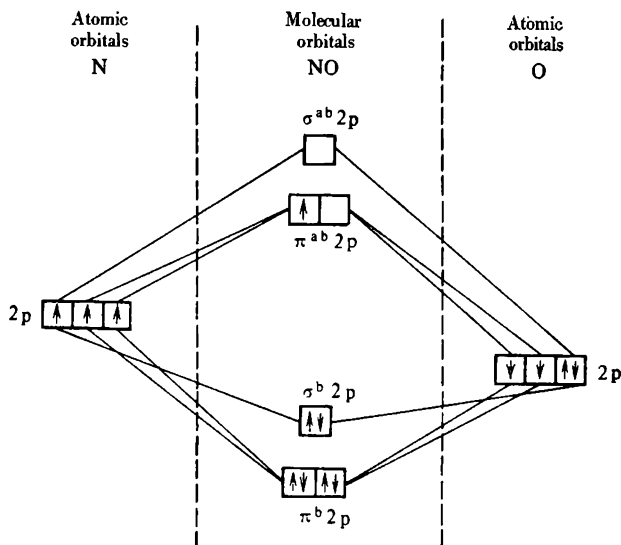
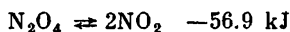


Fig. 12. Energy-level diagram showing the formation of an NO molecule

energy, the NO molecule is close to the molecular ion of oxygen O_2^+ (644 kJ/mol) in which the bond multiplicity is also 2.5 (see Vol. 1, p. 157).

When one electron is detached from the molecule NO, the ion NO^+ is formed containing no antibonding electrons; the bond multiplicity increases to three (six bonding electrons). Hence, the energy of dissociation of the NO^+ ion (1050 kJ/mol) is higher than that of the NO molecule and close to the relevant value for the CO molecule (1076 kJ/mol), in which the bond multiplicity is three.

Nitrogen dioxide NO_2 is a reddish-brown poisonous gas with a characteristic odour. It readily condenses into a reddish liquid (boiling point 21 °C) that gradually becomes lighter when cooled and freezes at -11.2 °C forming a colourless crystalline conglomeration. When gaseous nitrogen dioxide is heated, its colour, conversely, becomes more intense and at 140 °C it is almost black. The change in the colour of nitrogen dioxide with elevation of the temperature is attended by a change in its molecular mass. At a low temperature, the density of the vapour approximately corresponds to the double formula N_2O_4 (dinitrogen tetroxide). Elevation of the temperature is attended by diminishing of the vapour density, and at 140 °C the latter corresponds to the formula NO_2 . The colourless crystals existing at -11.2 °C and a lower temperature consist of N_2O_4 molecules. When heated, the N_2O_4 molecules dissociate with the formation of molecules of dark brown nitrogen dioxide, complete dissociation occurs at 140 °C. Thus, at temperatures ranging from -11.2 to 140 °C, the NO_2 and N_2O_4 molecules are in equilibrium with one another:

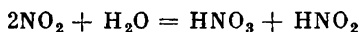


Above 140 °C, nitrogen dioxide dissociates into nitrogen monoxide and oxygen.

Nitrogen dioxide is a very vigorous oxidizing agent. Many substances can burn in an atmosphere of NO_2 , taking oxygen away from it. It oxidizes sulphur dioxide to the trioxide, this underlying the chamber process of producing sulphuric acid (see Sec. 17).

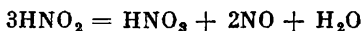
The vapour of NO_2 is poisonous. Its inhalation causes strong irritation of the respiratory ducts and may result in grave poisoning.

When dissolved in water, NO_2 reacts with it to form nitric and nitrous acids:



This is why nitrogen dioxide can be considered a mixed anhydride of these acids.

But nitrous acid is very unstable and rapidly decomposes:

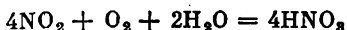


Consequently, the reaction of nitrogen dioxide with water, especially when the latter is hot, proceeds practically as follows:



which can be obtained by summing the two preceding equations after multiplying the first of them by three.

In the presence of air, the nitrogen monoxide formed is immediately oxidized to nitrogen dioxide, so that in this case the NO_2 in the long run is completely transformed into nitric acid:



This reaction is used in the modern processes for nitric acid production.

If we dissolve nitrogen dioxide in alkalis, a mixture of the salts of nitric and nitrous acids is obtained, for instance:

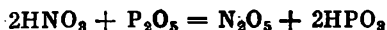


Dinitrogen trioxide N_2O_3 is a dark blue liquid decomposing into NO and NO_2 even at low temperatures. An equimolar mixture of NO and NO_2 when cooled again forms N_2O_3 :



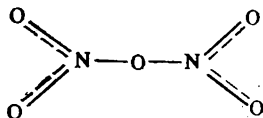
Dinitrogen trioxide is the acid anhydride of nitrous acid HNO_2 .

Dinitrogen pentoxide N_2O_5 is a white crystalline substance that already at room temperature gradually decomposes into NO_2 and O_2 . It can be obtained by reacting diphosphorus pentoxide with nitric acid:



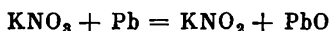
Dinitrogen pentoxide is a very strong oxidizing agent. Many organic substances ignite upon contact with it. Dinitrogen pentoxide dissolves well in water to form nitric acid.

In the solid state, N_2O_5 is formed by the nitrate ion NO_3^- and the nitronium ion NO_2^+ . The latter contains the same number of electrons as the CO_2 molecule and, like it, has a linear structure: $\text{O}=\text{N}^+=\text{O}$. In the vapour state, the N_2O_5 molecule is symmetrical. Its structure can be represented by the following valence formula in which the dash lines show the three-centre bonds (compare with the valence formula of the nitric acid molecule in Vol. 1, p. 146):



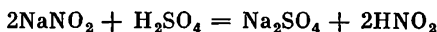
27. Nitrous Acid

If potassium or sodium nitrate is heated, the relevant salt loses part of its oxygen and transforms into a salt of nitrous acid HNO_2 . Decomposition proceeds more readily in the presence of lead that binds the liberated oxygen:

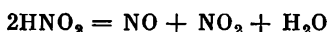


The salts of nitrous acid—**nitrites**—form crystals that are well soluble in water (except for silver nitrite). Sodium nitrite NaNO_2 is used in the production of various dyes.

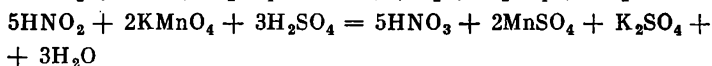
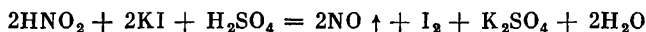
When a solution of a nitrite is reacted with dilute sulphuric acid free nitrous acid is obtained:



It is a weak acid ($K = 4 \times 10^{-4}$) and is known only in very dilute aqueous solutions. If the solution is concentrated or heated, the nitrous acid decomposes:



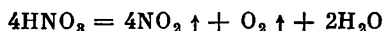
The oxidation number of nitrogen in nitrous acid is +3, i.e. it is intermediate between the minimum and maximum possible values of nitrogen's oxidation number. Consequently, HNO_2 exhibits oxidation-reduction duality. It is reduced (generally to NO) in reactions with reducing agents, and is oxidized to HNO_3 in reactions with oxidizing agents. The following reactions exemplify what has been said above:



28. Nitric Acid

Pure nitric acid HNO_3 is a colourless liquid with a density of 1.51 g/cm^3 freezing at -42°C into a transparent crystalline conglomeration. It "fumes" in the air like concentrated hydrochloric acid because its vapour forms minute drops of mist with the moisture in the air.

Nitric acid is not stable. Even under the influence of light, it gradually decomposes:



The rate of decomposition grows with an increase in the temperature and concentration of the acid. The liberated nitrogen dioxide dissolves in the acid and colours it reddish brown.

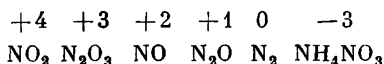
Nitric acid belongs to the group of the strongest acids. In dilute solutions, it decomposes completely into H^+ and NO_3^- ions.

A feature of nitric acid is its pronounced oxidizing power. Nitric acid is one of the most vigorous oxidizing agents. It oxidizes many non-metals into the relevant acids. For example, sulphur when boiled in nitric acid is gradually oxidized to sulphuric acid, and phosphorus to phosphoric acid. A glowing coal immersed in concentrated HNO_3 breaks out into a bright flame.

Nitric acid acts on almost all metals (except for gold, platinum, tantalum, rhodium, and iridium), transforming them into nitrates, and some of them into oxides.

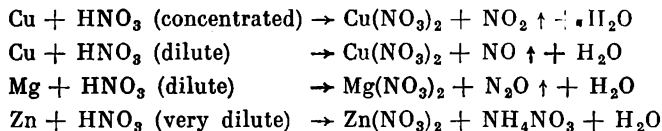
Concentrated HNO_3 passivates some metals. Already Lomonosov discovered that iron, which readily dissolves in dilute nitric acid, does not dissolve in cold concentrated HNO_3 . It was later found that nitric acid has a similar action on chromium and aluminium. These metals transform into a passive state under the action of concentrated nitric acid (see Vol. 1, Sec. 100).

The oxidation number of nitrogen in nitric acid is +5. When playing the role of an oxidizing agent, HNO_3 can be reduced to various products:



Which of these substances is formed, i.e. how far nitric acid is reduced in each case, depends on the nature of the reducing agent and on the conditions of the reaction, primarily on the acid concentration. The higher the concentration of the HNO_3 , the less is it reduced. Nitrogen dioxide NO_2 is liberated most frequently in reactions with concentrated acid. Nitrogen monoxide NO forms in reactions of dilute nitric acid with metals having a low activity such as copper. With more active metals—iron, zinc— N_2O is formed. Greatly diluted nitric acid reacts with active metals such as zinc, magnesium, and aluminium to form the ammonium ion which produces ammonium nitrate with the acid. Several products are usually formed simultaneously.

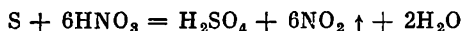
For purposes of illustration, below are given the skeleton equations of metal oxidation reactions involving nitric acid:



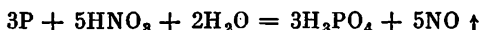
(The above equations are unbalanced, and the student is invited to balance them himself.)

When nitric acid acts on metals, hydrogen is not liberated as a rule.

When non-metals are oxidized, concentrated nitric acid, as with metals, is reduced to NO_2 , for example:

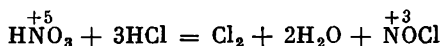


A more dilute acid is generally reduced to NO , for instance:

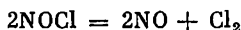


The above examples illustrate the most typical cases of the reaction of nitric acid with metals and non-metals. In general, however, oxidation-reduction reactions proceeding with the participation of HNO_3 are more involved.

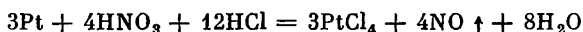
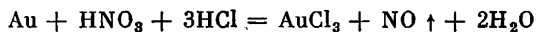
A mixture of one volume of nitric acid and three or four volumes of concentrated hydrochloric acid is known as *aqua regia* (the Latin for "royal water"). *Aqua regia* dissolves some of the metals that do not react with nitric acid, including the "royal metal"—gold. The explanation of its action is that the nitric acid oxidizes the hydrochloric acid with the liberation of free chlorine and the formation of nitrogen oxychloride or nitrosyl chloride NOCl :



Nitrosyl chloride is an intermediate of the reaction and decomposes:



The chlorine at the moment of its liberation consists of atoms, and this is exactly what explains the high oxidizing power of *aqua regia*. The reactions of oxidation of gold and platinum proceed basically as follows:



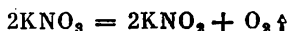
The gold(III) chloride and platinum(IV) chloride form the complex compounds $\text{H}[\text{AuCl}_4]$ and $\text{H}_2[\text{PtCl}_6]$ with the excess hydrochloric acid.

Nitric acid acts on many organic substances so that one or more hydrogen atoms in a molecule of an organic compound are displaced by nitrogroups $-\text{NO}_2$. This process is called **nitration** and is of great importance in organic chemistry.

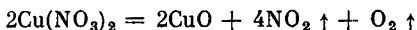
The electronic structure of the HNO_3 molecule was considered in Vol. 1, Sec. 44.

Nitric acid is one of the most important compounds of nitrogen. It is used in great amounts in the production of nitrogen fertilizers, explosives, and organic dyes; it is an oxidizing agent in many chemical processes, participates in the production of sulphuric acid by the chamber process, and is used in the manufacture of cellulose lacquers and varnishes and of cinema film.

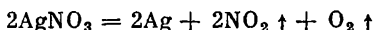
The salts of nitric acid are called **nitrates**. They all dissolve well in water, while when heated decompose with the liberation of oxygen, the nitrates of the most active metals transforming into nitrites:



The nitrates of most of the remaining metals decompose when heated into a metal oxide, oxygen, and nitrogen dioxide. For example:



Finally, the nitrates of the least active metals (for instance, of silver and gold) decompose when heated to the free metal:



Nitrates at a high temperature are vigorous oxidizing agents because they readily detach oxygen. Their aqueous solutions, on the contrary, do not virtually display oxidizing properties.

Of the greatest importance are the nitrates of sodium, potassium, ammonium, and calcium.

Sodium nitrate NaNO_3 is encountered in large amounts in nature only in Chile, and for this reason it is often called **Chile saltpetre**.

Potassium nitrate KNO_3 , or **saltpetre**, is also encountered in small amounts in nature, but is mainly prepared artificially by reacting sodium nitrate with potassium chloride.

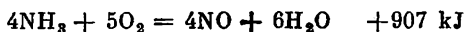
Both these salts are used as fertilizers, potassium nitrate containing two elements needed by plants: nitrogen and potassium. Sodium and potassium nitrates are also used in the manufacture of glass and in the food industry for preserving products.

Calcium nitrate $\text{Ca}(\text{NO}_3)_2$ is obtained in large amounts by the neutralization of nitric acid with lime. It is used as a fertilizer.

For **ammonium nitrate** NH_4NO_3 , see p. 72.

29. The Industrial Production of Nitric Acid

The modern industrial methods of producing nitric acid are based on the catalytic oxidation of ammonia by the oxygen of the air. In describing the properties of ammonia (see Sec. 23), it was indicated that it burns in oxygen, the products being water and free nitrogen. But in the presence of catalysts, the oxidation of ammonia by oxygen may proceed differently. If a mixture of ammonia and air is passed over a catalyst, at 750°C and a definite composition of the mixture the NH_3 is almost completely converted to NO :



The NO formed is easily transformed into NO_2 , and the latter reacts with water in the presence of the oxygen of the air to produce nitric acid (see Sec. 26).

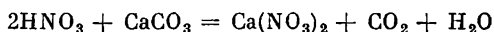
Platinum-based alloys are used as catalysts in the oxidation of ammonia.

The nitric acid produced by the oxidation of ammonia has a concentration not exceeding 60%. If necessary, it is concentrated.

The chemical industry markets dilute nitric acid with a concentration of 55, 47, and 45%, and concentrated acid—98 and 97%. The concentrated acid is transported in aluminium tank cars, and the dilute acid in cars with acid-resistant steel tanks.

30. Nitrogen Cycle in Nature

When organic substances decay, a considerable part of the nitrogen they contain transforms into ammonia, which under the influence of the **nitrifying** bacteria in the soil is oxidized to nitric acid. The latter, entering into a reaction with the carbonates in the soil, for example, with calcium carbonate CaCO_3 , forms nitrates:



A part of the nitrogen, however, is always liberated in decay into the atmosphere in the free state. Free nitrogen is also released in the burning of organic substances and of firewood, coal, and peat. Bacteria also exist that with a limited access of air can remove oxygen from nitrates, decomposing them with the liberation of free nitrogen. The activity of these **denitrifying** bacteria results in part of the nitrogen being converted from a form assimilable by green plants (nitrates) to an inaccessible one (free nitrogen). Thus, far from all the nitrogen in dead plants returns to the soil; part of it is gradually liberated in the free state.

The continuous depletion of mineral nitrogen compounds ought to have resulted in the complete cessation of life on Earth long ago if there were no processes in nature that made up for these losses. These processes include first of all the electric discharges occurring in the atmosphere during which a certain amount of nitrogen oxides is always formed. The latter combine with water into nitric acid that transforms into nitrates in the soil. Another source of replenishing of the nitrogen compounds in the soil is the vital activity of **nitrobacteria**, capable of assimilating the atmospheric nitrogen. Some of these bacteria settle on the roots of plants of the legume family causing the formation of characteristic nodules. This is why they have been named **nodule bacteria**. In assimilating atmospheric nitrogen, the nodule bacteria convert it into nitrogen compounds, while plants, in turn, convert the latter into proteins and other complex substances.

Consequently, there is a continuous nitrogen cycle in nature. But every year, the parts of plants richest in proteins, for example grain, are removed from fields with the harvest. This is why it is

necessary to introduce fertilizers into the soil that will make up for the withdrawal from it of the most important elements needed for the nutrition of plants.

The study of plant nutrition and the increase of crop yields by employing fertilizers is the subject of a special branch of chemistry called **agrochemistry**. Great contributions to the development of this science were made by the French scientist J. Boussingault, the German chemist J. Liebig, and the Russian scientist D. Pryanishnikov*.

PHOSPHORUS

31. Occurrence. Preparation and Properties

Phosphorus belongs to the quite widespread elements. Its content in the Earth's crust is about 0.1% (mass). Owing to its easy oxidability, phosphorus is not encountered in nature in the free state.

The most important of the natural compounds of phosphorus is calcium phosphate (or calcium orthophosphate) $\text{Ca}_3(\text{PO}_4)_2$, which in the form of the mineral **phosphorite** is sometimes found in large deposits. The largest phosphorite deposits in the USSR are in Southern Kazakhstan in the Kara-Tau Mountains. The mineral **apatite** containing CaF_2 or CaCl_2 in addition to $\text{Ca}_3(\text{PO}_4)_2$ is also encountered quite frequently. Enormous deposits of apatite were discovered in the twenties of the present century on the Kola Peninsula. This deposit is the largest in the world.

Phosphorus, like nitrogen, is needed by all living beings because it enters the composition of some proteins of both a vegetable and an animal origin. In plants, phosphorus is contained chiefly in the seed proteins, in animals—in proteins of milk, blood, brain, and nerve tissues. A large amount of phosphorus is also contained in the bones of vertebrates, mainly in the form of the compounds $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$ and $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCO}_3 \cdot \text{H}_2\text{O}$. Nucleic acids—complex organic polymer compounds found in all living organisms—contain phosphorus in the form of the acid residue of phosphoric

* Jean Batist Boussingault (1802-1887) was a member of the Paris Academy of Sciences from 1839. He discovered that all plants, except leguminous ones, take nitrogen from the soil, while the leguminous plants add nitrogen to it. He proved that green plants get their carbon from the carbon dioxide in the air.

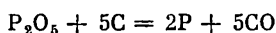
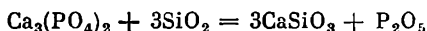
Justus Liebig (1803-1873) was a professor at the universities of Gissen (from 1824) and Munich (from 1852). From 1860, he was the president of the Bavarian Academy of Sciences. His main interest was in organic chemistry; in 1840, he advanced the theory of the mineral nutrition of plants that facilitated the widespread introduction of mineral fertilizers into agriculture.

Dmitri Nikolayevich Pryanishnikov (1865-1948), academician, Hero of Socialist Labour, Lenin and State Prize winner, was the founder and head of the Soviet school of agrochemists. He is the author of many scientific works, including works devoted to the nitrogen nutrition of plants.

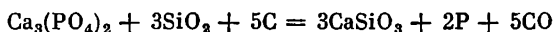
acid. Nucleic acids play a direct role in the transmission of hereditary properties of living cells.

Phosphorites and apatites are the starting material for the preparation of phosphorus and its compounds. The natural phosphorite or apatite is comminuted, mixed with sand and coal, and heated in electric furnaces without the access of air.

To understand how the reaction proceeds, let us conceive calcium phosphate as a compound of calcium oxide and phosphoric anhydride ($3\text{CaO} \cdot \text{P}_2\text{O}_5$); sand consists chiefly of silicon dioxide SiO_2 . At a high temperature, the silicon dioxide displaces the phosphoric anhydride and combines with the calcium oxide to form the readily fusible calcium silicate CaSiO_3 , while the phosphoric anhydride is reduced by the coal to free phosphorus:



Summation of these two equations yields:



The phosphorus is liberated in the form of a vapour that condenses in a receiver under water.

Phosphorus forms several allotropic modifications.

White phosphorus is obtained in the solid state when phosphorus vapour is rapidly cooled; its density is 1.83 g/cm^3 . Pure white phosphorus is absolutely colourless and transparent; the commercial product is usually yellowish and resembles wax in appearance. White phosphorus is brittle in the cold, but at a temperature above 15°C it becomes soft and can easily be cut with a knife.

White phosphorus oxidizes very rapidly in the air and glows in the dark. This explains the name "phosphorus", which is the Greek for "light bearing". When only slightly heated, for which purpose friction is sufficient, phosphorus ignites and burns, liberating a large amount of heat. It may ignite spontaneously in the air owing to the evolution of heat in oxidation. To protect white phosphorus from oxidation, it is kept under water—it does not dissolve in the latter. It does dissolve quite well in carbon disulphide.

White phosphorus has a molecular crystal lattice with the tetrahedral molecules of P_4 at its points. The bond strength between the atoms in these molecules is comparatively low. This explains the high chemical activity of white phosphorus.

White phosphorus is a strong poison that is mortal even in small doses.

If white phosphorus is heated for a long time at $250\text{--}300^\circ\text{C}$ without the access of air, it transforms into a different modification of the element having a red-purple colour and called red phosphorus. The

same transformation occurs, but very slowly, under the action of light.

Red phosphorus sharply differs in its properties from the white modification. It oxidizes very slowly in the air, does not glow in the dark, ignites only at 260 °C, does not dissolve in carbon disulphide, and is not poisonous. Its density is 2.0-2.4 g/cm³. The varying value of the density is due to the fact that red phosphorus consists of several forms. Their structure has not been established completely to date, but they are known to be polymeric substances.

When strongly heated, red phosphorus evaporates (sublimes) without melting. White phosphorus is obtained when the vapour is cooled.

Black phosphorus is formed from the white modification when it is heated to 200-220 °C under a very high pressure. It is similar in appearance to graphite, is greasy to the touch, and heavier than the other modifications; its density is 2.7 g/cm³. Black phosphorus is a semiconductor (see p. 204).

Phosphorus has a variety of applications. A large amount of it is used in the manufacture of matches.

The red modification is used in the match industry. It is contained in the compound applied to the sides of a matchbox or to the rubbing surface of a matchbook. The head of a match consists of a mixture of combustible substances with potassium chlorate and compounds catalyzing the decomposition of the salt (MnO₂, Fe₂O₃, etc.).

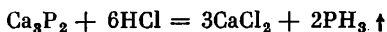
Besides the match industry, phosphorus has found application in metallurgy. It is used for the production of certain semiconductors—gallium phosphide GaP and indium phosphide InP. It is included in other semiconductors in very small amounts as an essential addition. It is also included in the composition of some metallic materials, for instance tin bronze.

When phosphorus burns, a thick white smoke is formed; it is therefore used to fill missiles (artillery shells, bombs, etc.) intended for the formation of a smokescreen. A large amount of phosphorus goes to produce organophosphorus preparations including very effective insecticides.

Free phosphorus is exceedingly active. It reacts directly with many elementary substances with the evolution of a large amount of heat. Phosphorus combines most readily with oxygen, then with the halogens, sulphur, and with many metals. In the latter case, **phosphides** such as Ca₃P₂ and Mg₃P₂ are formed similar to nitrides. All these properties manifest themselves especially sharply in white phosphorus; red phosphorus reacts less vigorously, while the black modification in general enters into a chemical reaction with difficulty.

32. Phosphorus Compounds with Hydrogen and the Halogens

With hydrogen, phosphorus forms gaseous **hydrogen phosphide** or **phosphine** PH_3 . It can be prepared by boiling white phosphorus with an alkali solution or by reacting hydrogen chloride with calcium phosphide Ca_3P_2 :



Phosphine is a colourless gas¹ with the odour of garlic; *it is very poisonous**. It burns in air to form diphosphorus pentoxide and water

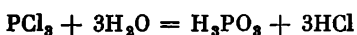


The basic properties of phosphine are weaker than those of its nitrogen counterpart—ammonia. It forms salts only with the strongest acids, for instance, HClO_4 and HCl . In these salts the **phosphonium** ion PH_4^+ is the cation. An example is **phosphonium chloride** PH_4Cl . Phosphonium salts are very unstable compounds. When contacted with water, they decompose into a hydrogen halide and phosphine.

Phosphorus combines directly with all the halogens with the evolution of a large amount of heat. Of practical importance are chiefly the compounds of phosphorus with chlorine.

Phosphorus trichloride PCl_3 is obtained when chlorine is passed over molten phosphorus. It is a liquid boiling at 75°C .

In water, PCl_3 completely hydrolyzes to form hydrogen chloride and phosphorous acid H_3PO_3 :



When chlorine is passed into phosphorus trichloride, **phosphorus pentachloride** PCl_5 is obtained. In ordinary conditions, it forms a solid white conglomerate. Phosphorus pentachloride is also decomposed by water with the formation of hydrogen chloride and phosphoric acid. Phosphorus forms similar compounds with bromine, iodine, and fluorine; for iodine, however, the compound PI_5 is unknown.

Phosphorus chlorides are employed in the synthesis of a variety of organic substances.

33. Oxides and Acids of Phosphorus

The most important oxides of phosphorus are P_2O_3 and P_2O_5 .

Diphosphorus trioxide or **phosphorous anhydride** P_2O_3 is obtained in the slow oxidation of phosphorus, or when phosphorus burns with

* A small amount of liquid diphosphine P_2H_4 whose vapour self-ignites in the air is sometimes formed simultaneously with phosphine.

an insufficient access of oxygen, as white crystals melting at 23.8°C . Its molecular mass at low temperatures corresponds to the formula P_4O_6 (tetraphosphorus hexoxide). When brought into contact with cold water, diphosphorus trioxide slowly reacts with it to form **phosphorous acid** H_3PO_3 . Both diphosphorous trioxide and phosphorous acid have strongly expressed reducing properties.

Diphosphorus pentoxide or **phosphoric anhydride** P_2O_5 is formed when phosphorus burns in the air or in oxygen as a white voluminous substance resembling snow. The density of its vapour corresponds to the formula P_4O_{10} .

Diphosphorus pentoxide combines greedily with water and is therefore used as a very strong dehydrating agent. In air, diphosphorus pentoxide attracts moisture and rapidly transforms into a deliquescent body of metaphosphoric acid.

Phosphoric Acids. Several acids correspond to diphosphorus pentoxide. The most important of them is orthophosphoric acid H_3PO_4 , which is generally called simply phosphoric acid. The other phosphoric acids are polymer compounds. In the anion of all phosphoric acids, the phosphorus atom, which is in the state of sp^3 hybridization, is surrounded by four oxygen atoms at the corners of a tetrahedron. Orthophosphoric acid is built of isolated tetrahedra, while in the other phosphoric acids the tetrahedra PO_4 are combined via oxygen atoms into aggregates containing from two to a very great number—of the order of 10^6 —of phosphorus atoms.

Orthophosphoric (phosphoric) acid H_3PO_4 forms colourless transparent crystals melting at 42.35°C . They dissolve very well in water.

Orthophosphoric acid does not belong to the strong acids. Its dissociation constants are $K_1 = 8 \times 10^{-3}$, $K_2 = 6 \times 10^{-8}$, and $K_3 = 10^{-12}$. Being tribasic, it forms three series of salts: normal salts and acid ones with one or two hydrogen atoms in the acid residue. The normal salts of phosphoric acid are called **phosphates (orthophosphates)**, the acid ones are **hydrogen phosphates**:

Na_3PO_4 ; $\text{Ca}_3(\text{PO}_4)_2$ —normal, or tertiary phosphates

Na_2HPO_4 ; CaHPO_4 —hydrogen, or secondary phosphates

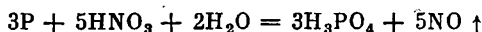
NaH_2PO_4 ; $\text{Ca}(\text{H}_2\text{PO}_4)_2$ —dihydrogen, or primary phosphates

Dihydrogen phosphates are soluble in water; of the hydrogen and normal phosphates, only the salts of the alkali metals and ammonium dissolve well.

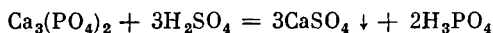
Phosphates hydrolyze in aqueous solutions. Solutions of normal salts of the alkali metals have a strongly alkaline reaction. For instance, the pH of a 1% solution of Na_3PO_4 is 12.1. The hydrolysis of acid salts is attended by dissociation of the acid residue (see Vol. 1, Sec. 92). This is why solutions of hydrogen phosphates of the alkali metals have a weakly basic reaction, and solutions of dihy-

drogen phosphates of these metals have a weakly acid one. For instance, the pH of a 1% solution of Na_2HPO_4 is 8.9, and of NaH_2PO_4 , 6.4.

In the laboratory, phosphoric acid can be prepared by oxidizing phosphorus with 30% HNO_3 . The reaction proceeds as follows:



Phosphoric acid is produced commercially by the extraction and thermal methods. The former is based on treating natural phosphates with sulphuric acid:

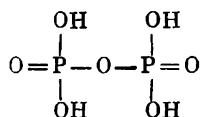


The phosphoric acid thus formed is filtered from the calcium sulphate and is concentrated by evaporation. The thermal method consists in reducing natural phosphates to free phosphorus, burning the latter, and dissolving the phosphoric anhydride obtained in water. The thermal phosphoric acid produced by this method has a high purity and concentration.

In addition to the production of fertilizers described in the following section, phosphoric acid is used in the preparation of reagents and many organic substances, and for providing protective coatings on metals. Calcium and ammonium phosphates are employed in the production of enamels and in the pharmaceutical industry.

All the other phosphoric acids are products of joining together of the PO_4 tetrahedra. The majority of these acids have not been recovered in the free state, but are known as mixtures, in aqueous solutions, or as salts. Depending on how the PO_4 groups are joined up into phosphate complexes, these acids are divided into **polyphosphoric** and **metaphosphoric** acids. Polyphosphoric acids and their salts—**polyphosphates**—are built of the chains $-\text{PO}_3-\text{O}-\text{PO}_3-$. In metaphosphoric acids and their salts—**metaphosphates**—the PO_4 tetrahedra form rings.

Of the polyphosphoric acids, only the simplest one—**diphosphoric** (or **pyrophosphoric**) acid— $\text{H}_4\text{P}_2\text{O}_7$ has been separated in the crystalline state. It forms colourless crystals melting at 61°C . The $\text{P}_2\text{O}_7^{4-}$ ion is built of two PO_4 tetrahedra with a common oxygen atom. The structural formula of diphosphoric acid is



Diphosphoric acid dissolves well in water and is somewhat stronger than H_3PO_4 (its dissociation constants are $K_1 = 1.4 \times 10^{-1}$, $K_2 = 10^{-2}$, $K_3 = 2 \times 10^{-7}$, $K_4 = 4 \times 10^{-10}$). Its salts are known as **diphosphates** (or **pyrophosphates**).

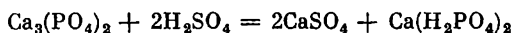
Metaphosphoric acids have the general formula $H_nP_nO_{3n}$, where n can have any value from 3 to 8. Frequently, however, their composition is expressed by the simplest formula HPO_3 . These acids are vitreous substances. In solution, they acquire the form of polymers having a cyclic structure. With time, the rings break open, and chain polyphosphoric acids are formed. *Metaphosphoric acids are poisonous.* Salts of metaphosphoric acids—**metaphosphates**—are known. Some of them have been separated as crystals, for example, $Na_3P_3O_9$, $Na_4P_4O_{12}$, and $Ca_3(P_3O_9)_2$. Metaphosphates are used for softening water and lowering its corroding activity, for removing scale from steam boilers, and are also included in the composition of certain detergents.

34. Mineral Fertilizers

We have mentioned above that the introduction into the soil of the elements needed for the growth and development of plants is of tremendous importance for raising the yields of agricultural crops. These elements are introduced into the soil in the form of **organic** (manure, peat, etc.) and **mineral** (products of the chemical processing of mineral raw materials) **fertilizers**. Their production is one of the most important branches of the chemical industry.

The most important mineral fertilizers are phosphorus ones. Natural phosphorus compounds—phosphorites and apatites—contain phosphorus in the form of the insoluble normal phosphate $Ca_3(PO_4)_2$ that is poorly assimilated by plants. To prepare readily assimilable fertilizers, phosphorites are processed chemically to convert the normal salt into the acid one. The most important phosphorus fertilizers—superphosphate, double superphosphate, and precipitate—are produced in this way.

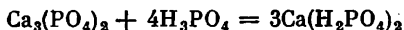
To manufacture **superphosphate**, finely comminuted natural phosphorite is mixed with sulphuric acid. The mixture is vigorously agitated and charged into continuously operating chambers where the reaction terminates:



The result is a mixture of calcium sulphate with dihydrogen phosphate $Ca(H_2PO_4)_2$ that dissolves comparatively readily in water. It is this mixture in the granulated or comminuted form that is called superphosphate.

Simple superphosphate is a fertilizer with a comparatively low content of nutritious substances.

Double superphosphate is the product of decomposition of natural phosphate by phosphoric acid:



Double superphosphate contains no calcium sulphate, which lowers the cost of its transportation and introduction into the soil.

Precipitate is a phosphorus fertilizer including calcium hydrogen phosphate CaHPO_4 , which is insoluble in water, but dissolves when introduced into acid soils.

The phosphorus fertilizers described above are called **single** ones because they contain only one of the elements needed by plants. More prospective are **compound** or **mixed** fertilizers containing several nutritious substances. Such fertilizers include Ammophos and Nitrophoska.

Ammophos is prepared by reacting phosphoric acid with ammonia. Depending on the degree of neutralization, either monoammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$ or diammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$ is formed.

Nitrophoska is a triple fertilizer containing nitrogen, phosphorus, and potassium. It is prepared by fusing ammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$, ammonium nitrate NH_4NO_3 , and potassium chloride (or sulphate).

Before the October Revolution, virtually no mineral fertilizers were produced in Russia; the entire output of several small plants in 1913 was only 89 000 tonnes. The erection of new plants began in the USSR only in 1925-1926 and was conducted in the following period on a large scale.

In 1977, the output of mineral fertilizers was 96.7 million tonnes. Together with the growth in the quantity of fertilizers produced, their assortment is also being improved. It is planned to considerably step up the production of the most effective combined and compound fertilizers.

For **microfertilizers**, see p. 245.

ARSENIC, ANTIMONY, BISMUTH

35. Arsenic (*Arsenicum*)

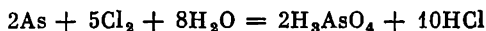
Arsenic occurs in nature chiefly in compounds with metals or sulphur and only rarely in the free state. The arsenic content in the Earth's crust is 0.0005% (mass).

Arsenic is generally prepared from **mispickel** (arsenopyrite) FeAsS . When heated in air, diarsenic trioxide As_2O_3 is formed, which is further reduced with carbon to free arsenic.

Like phosphorus, arsenic exists in several allotropic modifications. The most stable of them in ordinary conditions and when heated is **metallic** or **gray** arsenic. It forms a steel-gray brittle crystalline solid with a metallic lustre on a fresh fracture. The density of gray arsenic is 5.72 g/cm^3 . When heated under atmospheric pressure, it

sublimes. Unlike the other modifications, gray arsenic possesses metal conductance.

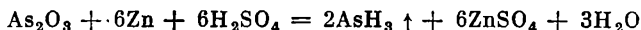
Arsenic does not dissolve in water. It oxidizes very slowly in air at room temperature, but when heated strongly it burns and forms the white oxide As_2O_3 , emitting a characteristic garlic-like odour. At an elevated temperature, arsenic reacts directly with many elements. Strong oxidizers transform it into arsenic acid, for instance:



Both free arsenic and all of its compounds are strong poisons.

Arsenic exhibits the oxidation states +5, +3, and -3 in its compounds.

Arsenic trihydride or **arsine** AsH_3 is a colourless very poisonous gas with a characteristic garlic-like odour and dissolves only slightly in water. Arsine is formed when all arsenic compounds are reduced with nascent hydrogen. For example:

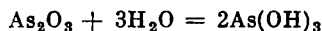


Arsine is comparatively unstable and when heated readily decomposes into hydrogen and free arsenic. This property of arsine is used for detecting arsenic in various substances. The substance being analysed is treated with a reducing agent and if it contains a compound of arsenic or arsenic in the free state, AsH_3 is formed. Next the reduction products are heated, the arsine decomposes, and the liberated arsenic forms a characteristic black glittering deposit on the cold parts of the apparatus called an "arsenic mirror".

Arsenic forms compounds known as **arsenides** with some metals. Many arsenides can be considered as the products of displacement of hydrogen in arsine by metal atoms, for instance, Cu_3As and Ca_3As_2 .

Arsenic produces two oxides with oxygen: As_2O_3 and As_2O_5 .

Diarsenic trioxide or **arsenous anhydride** As_2O_3 is obtained when arsenic burns in air or when arsenic ores are calcined. It is a white substance called **white arsenic**. Diarsenic trioxide dissolves rather poorly in water: a solution saturated at 15°C contains only 1.5% As_2O_3 . When diarsenic trioxide dissolves in water, it reacts with it to form arsenic(III) hydroxide or arsenous acid:



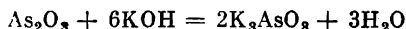
Arsenic(III) hydroxide is amphoteric, but its acid properties predominate.

Arsenous acid H_3AsO_3 has not been obtained in the free state and is known only in an aqueous solution in which equilibrium sets in:



This equilibrium is greatly shifted to the right, i.e. the predominating form is metaarsenous acid HAsO_2 . The dissociation constant of this acid is $K = 6 \times 10^{-10}$. When alkalis react with As_2O_3 ,

salts of arsenous acid called **arsenites** are obtained, for instance:



The compounds of arsenic(III) display reducing properties; when they are oxidized, compounds of arsenic(V) are obtained.

Arsenic acid H_3AsO_4 in ordinary conditions is in the solid state; it dissolves well in water. Its strength is almost equal to that of phosphoric acid. Its salts—**arsenates**—are very similar to the relevant phosphates. Meta- and diarsenic acids are also known. The calcination of arsenic acid yields **diarsenic pentoxide**, or **arsenic anhydride** As_2O_5 in the form of a white vitreous mass.

The acid properties of arsenic acid are much more pronounced than those of arsenous acid. This is a particular case of the general law according to which an increase in the oxidation number of an element is attended by a growth in the acid properties of its hydroxides and weakening of the basic ones (see p. 37).

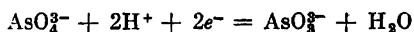
Being tribasic, arsenic acid forms normal (**arsenates**) and acid (**hydrogen and dihydrogen arsenates**) salts, for instance, Na_3AsO_4 , Na_2HAsO_4 , and NaH_2AsO_4 .

In an acid medium, arsenic acid and arsenates exhibit oxidizing properties.

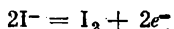
It was noted in Vol. 1, Sec. 99, that the electrode potentials of processes occurring with the participation of water, hydrogen ions, or hydroxide ions have higher values when the acidity of the solution is greater. In other words, if water and its dissociation products participate in an electrochemical process, an oxidizing agent exhibits its oxidizing properties more strongly in an acid medium, and a reducing agent exhibits its reducing properties more strongly in an alkaline medium. This general law can be illustrated quite well using arsenic compounds as an example. Arsenic acid and its salts in an acid medium react with reducing agents, transforming into arsenous acid or arsenites. For instance:



Here, the reduction process is described by the equation:

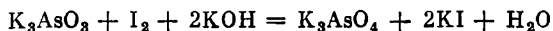


and the oxidation process by the equation:

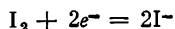


Reduction can be seen to proceed with the participation of water and H^+ ions, and oxidation without their participation. Consequently, the pH of the medium affects only the potential of the reduction process: the lower the pH, the higher is this potential and the stronger an oxidizing agent is the ion AsO_4^{3-} .

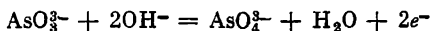
At the same time, in an alkaline medium, arsenous acid and its salts are readily oxidized, transforming into arsenates, for example:



Here, the reduction process is described by the equation:



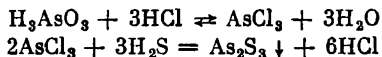
and the oxidation process by the equation



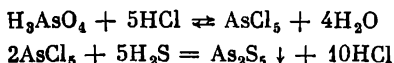
In this case, the water and OH^- ions participate only in oxidation. Hence, here the pH of the medium affects only the potential of the oxidation process: the higher the pH, the lower is this potential and the stronger a reducing agent is the AsO_3^{3-} ion.

We thus see that the direction of oxidation-reduction reactions proceeding with the participation of water and its dissociation products can change when passing from an acid medium to an alkaline one.

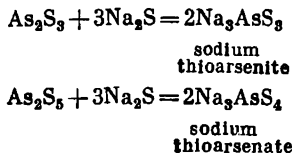
Sulphides of Arsenic. If we pass hydrogen sulphide into an arsenous acid solution acidified with hydrogen chloride, a yellow precipitate of diarsenic trisulphide As_2S_3 is formed that does not dissolve in hydrochloric acid. The reactions can be expressed by the equations



A yellow precipitate of diarsenic pentasulphide As_2S_5 can be prepared in a similar way by acting with hydrogen sulphide on a solution of arsenic acid in the presence of hydrogen chloride:



When arsenic sulphides react with the sulphides of the alkali metals Na_2S , K_2S , or with ammonium sulphide $(\text{NH}_4)_2\text{S}$, salts of thioarsenous (H_3AsS_3) and thioarsenic (H_3AsS_4) acids are formed that are soluble in water. The acids H_3AsS_3 and H_3AsS_4 can be considered as the corresponding oxygen-containing acids of arsenic in which the entire oxygen is displaced by sulphur:



The use of free arsenic is limited. But arsenic compounds are employed in medicine, and also in agriculture as insecticides, i.e. as means for destroying harmful insects.

Diarsenic trioxide is used as a poison for rodents.

36. Antimony (*Stibium*)

Antimony generally occurs in nature as sulphur compounds in the form of stibnite or antimonite Sb_2S_3 . Although the antimony content in the Earth's crust is comparatively low (0.000 05 % (mass)), antimony has been known since ancient times. This is explained by the widespread occurrence of stibnite in nature and the ease with which antimony can be extracted from it. When roasted in air, stibnite transforms into distibium trioxide Sb_2O_3 from which antimony is prepared by reduction with carbon (coal).

Free antimony forms silvery crystals with a metallic lustre and having a density of 6.68 g/cm^3 . Reminding one of a metal in its appearance, crystalline antimony is distinguished by its brittleness and conducts heat and electric current much more poorly than the ordinary metals. Antimony has other allotropic modifications in addition to the crystalline form.

Antimony is introduced into certain alloys to make them harder. An alloy consisting of antimony, lead, and a small amount of tin is called **type metal** and is used to make type for printing shops. An alloy of antimony with lead (from 5 to 15 % of Sb) goes to make the plates of lead accumulators, plates and pipes for the chemical industry. Antimony is also used as an addition to germanium for imparting definite semiconductor properties to it.

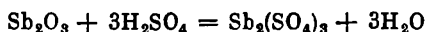
In tsarist Russia, notwithstanding the existence of a raw material base, no antimony was produced. The production of antimony from local ores was begun only after the October Revolution.

Antimony greatly resembles arsenic in its compounds, but differs from it in its more pronounced metallic properties.

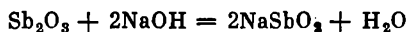
Stibine, or **antimony hydride** SbH_3 is a poisonous gas formed in the same conditions as arsine. When heated, it decomposes into antimony and hydrogen even more readily than arsine.

Antimony forms compounds with metals—**antimonides**—that can be considered as the products of displacement of the hydrogen in stibine by metal atoms. In these compounds, antimony, as in SbH_3 , has an oxidation number of -3 . Some antimonides such as AlSb , GaSb , and InSb have semiconductor properties and are used in the electronic industry.

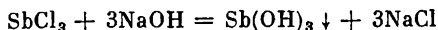
Diantimony trioxide, or **antimonous anhydride** Sb_2O_3 is a typical amphoteric oxide with a certain predomination of basic properties. In strong acids, for example, sulphuric acid and hydrogen chloride, diantimony trioxide dissolves to form salts of antimony(III):



Diantimony trioxide also dissolves in alkalis to form salts of antimonous H_3SbO_3 or metaantimonous HSbO_2 acid. For instance:

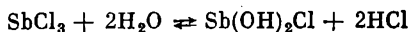


Antimonous acid, or **antimony(III) hydroxide** Sb(OH)_3 is obtained as a white precipitate when salts of antimony(III) are reacted with alkalis:

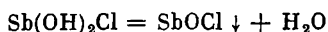


The precipitate dissolves readily both in an excess of the alkali and in acids.

The salts of antimony(III), as salts of a weak base, hydrolyze in an aqueous solution to form basic salts:



The resulting basic salt $\text{Sb(OH)}_2\text{Cl}$ is unstable and decomposes with the detachment of a water molecule:



The group SbO in the salt SbOCl plays the role of a monovalent metal and is known as **antimonyl**. The basic salt itself is called **antimonyl chloride** or **antimony(III) oxychloride**.

Diantimony pentoxide, or **antimonic anhydride** Sb_2O_5 has chiefly acid properties. **Antimonic acid** existing in several forms in an aqueous solution corresponds to it. The salts of antimonic acid are named **antimonates**.

The **antimony sulphides** Sb_2S_3 and Sb_2S_5 are similar in their properties to the relevant arsenic sulphides. They are orange-red substances dissolving in alkali metal and ammonium sulphides with the formation of thiosalts. Antimony sulphides are used in the production of matches and in the rubber industry.

37. Bismuth (*Bismuthum*)

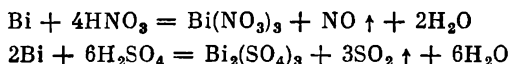
The last member of the subgroup, bismuth, is characterized by the predominance of metallic properties over non-metallic ones, and can be treated as a metal.

Bismuth is rather scarce in nature. Its content in the Earth's crust is 0.000 02% (mass). It occurs both in the free state and in compounds—**bismuth ochre** or **bismite** Bi_2O_3 and **bismuth glance** or **bismuthinite** Bi_2S_3 .

Bismuth in the free state is a lustrous pinkish-white brittle metal with a density of 9.8 g/cm³. It is used both in the pure state and in alloys. Pure bismuth finds its chief use in power-producing nuclear reactors as a heat-carrying agent. It forms fusible alloys with some metals. For instance, an alloy of bismuth with lead, tin, and cadmium melts at 70 °C. Such alloys are used, particularly, in automatic fire extinguishers whose functioning is based on the melting of a plug made from such an alloy. They are also used as solders.

Bismuth does not oxidize in the air at room temperature, but burns when heated, forming bismuth(III) oxide Bi_2O_3 . Hydrogen chloride

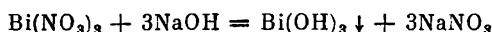
and dilute sulphuric acid do not react with bismuth. It dissolves in nitric acid of low concentration and in hot concentrated sulphuric acid:



Bismuthine, or **bismuth hydride** BiH_3 is very unstable and decomposes even at room temperature.

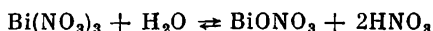
Bismuth(III) oxide Bi_2O_3 forms when bismuth is calcined in air, and also when bismuth nitrate decomposes. It is basic in nature and dissolves in acids to form salts of bismuth(III).

Bismuth(III) hydroxide $\text{Bi}(\text{OH})_3$ is obtained as a white precipitate when alkalis react with dissolved bismuth salts:



Bismuth(III) hydroxide is a very weak base. This is why the salts of bismuth(III) are readily hydrolyzed, transforming into basic salts that are poorly soluble in water.

Bismuth(III) nitrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ crystallizes from the solution obtained as a result of the reaction of bismuth with nitric acid. It dissolves in a small amount of water acidified with nitric acid. Dilution of the solution with water is attended by hydrolysis and precipitation of the basic salts whose composition depends on the conditions. Often a salt having the composition BiONO_3 is formed. The radical BiO —**bismuthyl**—plays the role of a monovalent metal:



Bismuth(III) chloride BiCl_3 forms hygroscopic crystals hydrolyzed by water to bismuthyl chloride BiOCl .

Bismuth(III) sulphide Bi_2S_3 forms as a black-reddish brown precipitate when hydrogen sulphide reacts with solutions of bismuth salts. The precipitate does not dissolve in sulphides of the alkali metals and ammonium: unlike arsenic and antimony, bismuth forms no thiosalts.

Compounds of bismuth(III) are used in medicine and in the veterinary science.

Compounds of bismuth(V) can be prepared by acting with very strong oxidizing agents on compounds of bismuth(III). The most important of them are **bismuthates**—salts of bismuth acid, which has not been prepared in the free state, for instance potassium bismuthate KBiO_3 . These compounds are very strong oxidizing agents.

5

THE MAIN SUBGROUP OF GROUP FOUR

The main subgroup of Group IV of the periodic table includes five elements—carbon, silicon, germanium, tin, and lead.

The size of the atoms grows when going from carbon to lead. It should therefore be expected that the ability to attach electrons and, consequently, the non-metallic properties will weaken, while the readiness to give up electrons will grow. Indeed, already germanium exhibits metallic properties, while in tin and lead they predominate over the non-metallic ones. Thus, only the first two members of Group IV are non-metals, germanium is included among both metals and non-metals, while tin and lead are metals.

Table 6

Selected Properties of Carbon and Its Analogues

	Carbon*	Silicon	Germa- nium	Tin	Lead
Configuration of outer electron layer of atom	$2s^2 2p^2$	$3s^2 3p^2$	$4s^2 4p^2$	$5s^2 5p^2$	$6s^2 6p^2$
Ionization energy of atom $E \rightarrow E^+$, eV	11.26	8.15	7.90	7.34	7.42
Relative electronegativity	2.5	1.8	1.8	1.8	1.9
Atomic radius, nm	0.077	0.134	0.139	0.158	0.175
Standard enthalpy of atomization at 25°C, kJ per mole of atoms	715.0	451.9	379.1	302.1	195.0
Melting point, °C	3750**	1420***	936	231.9	327.4
Boiling point, °C	...	3300	2850	2620	1745
Density, g/cm ³	Diamond 3.52 Graphite 2.26	2.33***	5.32	White 7.29 Gray 5.85	11.34

* In the standard state, carbon is in the form of graphite.

** At a pressure of 12 MPa.

*** Crystalline silicon.

Oxidation states of $+2$ and $+4$ are characteristic of the elements of this groups. Compounds of carbon and silicon in which their oxidation state is $+2$ are few in number and have a comparatively low stability.

Selected properties of the elements of the main subgroup of Group IV and the elementary substances they form are given in Table 6.

CARBON (*CARBONEUM*)

38. Occurrence

Carbon occurs in nature both in the free state and in the form of numerous compounds. Free carbon is encountered as diamond and graphite. Diamonds form separate crystals or intergrowths of a small size whose mass usually ranges from thousandths to tenths of a gram. The greatest of all found diamonds weighed 621.2 g. The crystals sometimes have a colour due to impurities. The greatest diamond deposits are found in Africa (Zair, the Union of South Africa), in Brazil, and in India.

The major graphite deposits were formed as a result of the action of high temperatures and pressures on coal. Graphite deposits are encountered in various regions of the USSR.

Charcoal, also consisting of carbon, is prepared artificially. Substances are encountered in nature, however, that are close in their composition to charcoal. These are the various kinds of mineral coal that form thick deposits at many places on the Earth. Some coals contain up to 99% of carbon.

Carbon compounds are very widespread. In addition to mineral coal, the Earth contains large accumulations of petroleum, which is a complex mixture of various carbon-containing compounds, mainly hydrocarbons. Salts of carbonic acid, especially calcium carbonate, are encountered in enormous amounts in the Earth's crust. The air always contains carbon dioxide. Finally, plants and animals consist of substances in whose formation carbon plays the chief role. Thus, this element is among the most widespread ones on the Earth, although its total content in the Earth's crust is only about 0.1% (mass).

Carbon occupies an absolutely exclusive place among the elements in the number and diversity of its compounds. The number of carbon compounds that have been studied to date is assumed to be about two million, whereas the number of compounds of all the other elements taken together totals only hundreds of thousands.

The diversity of the carbon compounds is explained by the ability of its atoms to combine with one another into long chains or rings (see Sec. 48).

39. Allotropy of Carbon

In the free state, carbon is known in the form of diamond crystallizing in the cubic system, and graphite belonging to the hexagonal system. Such forms of it as charcoal, coke, and carbon black have an unordered structure. Two other modifications of carbon—**carbine** and **polycumulene**—have been synthesized. They consist of linear chain polymers of the type $\dots-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\dots$ or $\dots=\text{C}=\text{C}=\text{C}=\dots$. Carbine has semiconductor properties. When strongly heated without the access of air, it transforms into graphite.

Diamond is a colourless transparent substance that refracts light rays exceedingly strongly. It crystallizes in a cubic face-centered lattice. One half of the atoms occupy the corners and centres of the faces of one cube, and the other half—the corners and centres of the faces of another cube displaced relative to the first one in the direction of its spatial diagonal. The carbon atoms in diamond are in the state of sp^3 hybridization and form a three-dimensional tetrahedral lattice in which they are bonded to one another by means of covalent bonds*. The distance between the atoms in the tetrahedra is 0.154 nm. The structure of diamond is shown in Fig. 13.

Of all elementary substances, diamond has the greatest number of atoms per unit volume—the carbon atoms are packed very tightly in diamond. This, together with the high bond strength in the carbon tetrahedra, underlies the fact that the hardness of diamond is superior to that of all known substances. This is why it is widely used in industry, almost 80% of all diamonds extracted are used for technical purposes. Diamond is used for processing various hard materials for drilling rock. Though it is very hard, diamond is brittle. The powder obtained in the comminution of diamond goes to polish precious stones and diamonds themselves. Properly cut and polished transparent diamonds are used in jewelry.

Owing to the high value of diamonds, many attempts were made to produce them artificially from graphite. For a long time, however, these attempts were unsuccessful. Only in 1955, using a very high pressure (of the order of 10^{10} Pa) and prolonged heating at about 3000 °C, did American and simultaneously Swedish scientists succeed in producing synthetic diamonds. A method of producing synthetic diamonds was also developed in the USSR, and their

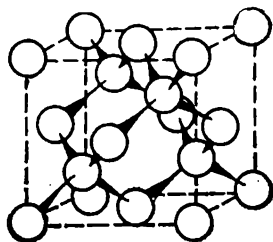


Fig. 13. The structure of diamond
The arrows show the bonds
between the atoms in the
tetrahedra

* Such a tetrahedral bonding is also characteristic of saturated hydrocarbons and their derivatives (p. 124).

commercial production was begun in 1961. In addition, in 1969, filamentary diamond crystals were synthesized in the USSR at a conventional pressure. The filamentary crystals or "whiskers" have a structure virtually deprived of defects, and are featured by a very high strength.

When calcined in oxygen, diamond burns and forms carbon dioxide. If diamond is strongly heated without the access of air, it transforms into graphite.

Graphite consists of dark-gray crystals with a slight metallic lustre. It has a layer lattice. All the carbon atoms here are in the state of sp^2 hybridization. Each of them forms three covalent sigma bonds with its neighbours, the angles between the directions of the bonds being 120 degrees. The result is the formation of a plane lattice consisting of regular hexagons with the carbon atom nuclei at their corners. The distance between adjacent nuclei is 0.1415 nm.

Three electrons of each carbon atom participate in the formation of the sigma bonds. The fourth electron of the outer layer occupies the $2p$ orbital that does not take part in hybridization. Such non-hybrid electron clouds of the carbon atoms are oriented at right angles to the plane of the layer and, overlapping one another, form delocalized pi bonds*. The structure of graphite is shown in Fig. 14.

The adjacent layers of the carbon atoms in a graphite crystal are quite far from one another (0.335 nm). This points to the low strength of the bond between carbon atoms in different layers. Adjacent layers are bonded to one another chiefly by van-der-Waals forces, but the bond partially has a metallic nature, i.e. is due to "collectivization" of the electrons by all the atoms of the crystal**. This explains the comparatively high electrical conductance and thermal conductance of graphite not only in the direction of the layers, but also in one perpendicular to them.

The structure of graphite considered above underlies the great anisotropy of its properties. For instance, the thermal conductivity of graphite in the direction of the layer planes is $4.0 \text{ J}/(\text{cm} \cdot \text{s} \cdot \text{K})$, while in the perpendicular direction it is $0.79 \text{ J}/(\text{cm} \cdot \text{s} \cdot \text{K})$. The electrical resistance of graphite perpendicular to its layers is 10^4 times greater than in their direction.

The individual layers of atoms in a graphite crystal that are bonded to one another comparatively weakly, readily separate. This explains the low mechanical strength of graphite. If we pass a piece of graphite over paper, minute graphite crystals having the form of scales adhere to the paper, leaving a gray line on it. This is why graphite is used for making pencils.

* The sigma and pi bonds in a benzene molecule are formed in a similar way. This system of bonds will be treated in greater detail in Sec. 45.

** The nature of the metallic bond is dealt with in Sec. 76.

Graphite does not ignite in the air even when strongly heated, but readily burns in pure oxygen, transforming into carbon dioxide.

Owing to its electrical conductance, graphite is employed for making electrodes. A mixture of graphite with clay goes to fabricate refractory crucibles for melting metals. Graphite mixed with oil is an excellent lubricant because its scales fill the irregularities of the material to create a smooth surface facilitating sliding. Graphite is also used as a neutron moderator in nuclear reactors.

In addition to natural graphite, artificial graphite is also used in industry. It is chiefly prepared from the best grades of coal. Conversion occurs at temperatures of about 3000°C in electrical furnaces without the access of air. Natural and, especially, artificial graphite is used to make materials employed in the chemical industry. Owing to their high chemical stability, they are used for furnace linings, pipes, etc.

Graphite is stable thermodynamically within a broad range of temperatures and pressures, particularly in ordinary conditions.

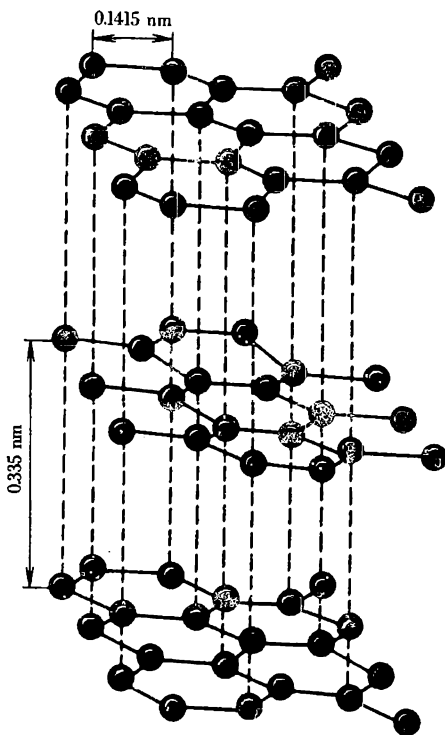


Fig. 14. The structure of graphite

Consequently, when calculating the thermodynamical quantities for carbon, graphite is adopted as its standard state. Diamond is thermodynamically stable only at high pressures (above 10^9 Pa). The rate of transformation of diamond into graphite, however, becomes appreciable only at temperatures above 1000°C . At 1750°C , diamond transforms rapidly into graphite.

"Amorphous" Carbon. When carbon-containing compounds are heated without the access of air, a black substance separates from them that is called amorphous carbon or simply carbon. This carbon consists of very minute crystals with the unordered structure of graphite. Carbon dissolves in many molten metals such as iron, nickel, and platinum. The density of this carbon varies from 1.8 to 2.1 g/cm^3 .

Amorphous carbons differ noticeably in their properties depending on what substance they have been prepared from and how this was done. In addition, they always contain impurities that greatly affect their properties. The most important technical grades of amorphous carbon are coke, charcoal, bone charcoal, and carbon black.

Coke is produced by the dry distillation of bituminous coal. It is mainly used in metallurgy in smelting metals from their ores.

Charcoal is obtained when wood is heated without the access of air, the valuable products of dry distillation such as methyl alcohol and acetic acid also being collected. Charcoal is used in metallurgy and in forging.

Owing to its porous structure, charcoal has a high adsorptivity.

Let us perform the following experiment to observe the adsorption of gases by charcoal. We fill a glass tube with ammonia and lower its open end into a vessel with mercury (Fig. 15). We next heat a piece of charcoal on a burner, immerse it in the mercury, and bring it under the open end of the tube with ammonia. The charcoal floats to the surface of the mercury in the tube, and the mercury immediately begins to rise owing to the ammonia being adsorbed by the charcoal.

Activated carbons (Vol. 1, p. 336) adsorb gases especially well. They are used to adsorb the

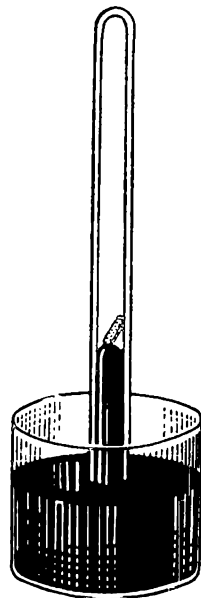


Fig. 15. Instrument for demonstrating how charcoal adsorbs ammonia

vapours of volatile liquids from the air and gas mixtures, in gas masks, and also as a catalyst in certain chemical production processes.

Amorphous carbon is capable of adsorbing not only gases, but also solutes. This was discovered at the end of the 18th century by the Russian academician T. Lovits.

Bone charcoal (or **boneblack**) is prepared by charring degreased bones. It contains from 7 to 11% of carbon, about 80% of calcium phosphate, and other salts. Bone charcoal is distinguished by its very high adsorptivity, especially with respect to organic dyes, and is used to remove various pigments from solutions.

Carbon black is the purest amorphous carbon. It is produced on a commercial scale by the thermal decomposition of methane, and also by burning substances rich in carbon such as pitch and turpentine with an inadequate supply of air. Carbon black is used as a black paint (India ink, printer's ink), and also in the rubber industry as an important component of rubber.

40. Chemical Properties of Carbon. Carbides

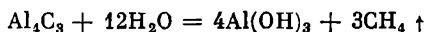
Amorphous carbon, graphite, and especially diamond are all inert at low temperatures. Heating increases their activity: amorphous carbon readily combines with oxygen and is a good reducing agent. The most important process in metallurgy—the smelting of metals from their ores—is achieved by reducing metal oxides with carbon (or carbon monoxide).

With oxygen, carbon forms carbon dioxide CO_2 and carbon monoxide CO .

At very high temperatures, carbon combines with hydrogen, sulphur, silicon, boron, and many metals. Amorphous carbon enters into the reaction more readily than graphite, and moreover than diamond.

Compounds of carbon with metals and other elements that are electropositive with respect to carbon are known as **carbides**. They are obtained by calcination of the metals or their oxides with carbon.

Carbides are crystalline bodies. The nature of the chemical bond in them may vary. For example, many carbides of metals of the main subgroups of Groups I, II, and III of the periodic table are salt-like compounds with an ionic bond predominating. Among them are aluminium carbide Al_4C_3 and calcium carbide CaC_2 . The former can be considered as the product of the substitution of hydrogen by a metal in methane CH_4 , and the latter in acetylene C_2H_2 . Indeed, aluminium carbide reacts with water to form methane:



and calcium carbide reacts with water to form acetylene:



In silicon carbide SiC (see Sec. 64) and tetraboron carbide B_4C , the bond between the atoms is covalent. These substances are hard, refractory, and chemically inert.

Most metals of the secondary subgroups of Groups IV-VIII form carbides in which the bond is close to a metallic one (see Sec. 76), owing to which these carbides in some respects are similar to metals, for instance they are good electrical conductors. They are also characterized by a great hardness and refractoriness. Carbides of this group are used in a number of branches of industry.

Most of the valuable properties of irons and steels are due to the presence in them of iron carbide Fe_3C (see Sec. 124).

41. Carbon Dioxide. Carbonic Acid

Carbon dioxide CO_2 is constantly formed in nature in the oxidation of organic substances (the decay of vegetable and animal remains, respiration, the burning of fuel). It is liberated in large amounts from volcanic fissures and from the waters of mineral springs.

Carbon dioxide is generally prepared in the laboratory by reacting marble CaCO_3 with hydrogen chloride in a Kipp gas generator:



Large amounts of carbon dioxide are obtained in industry in the calcination of limestone:

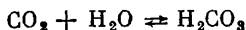


Carbon dioxide in conventional conditions is a colourless gas about 1.5 times heavier than air, owing to which it can be poured like a liquid from one vessel into another. The mass of one litre of CO_2 in standard conditions is 1.98 g. The solubility of carbon dioxide in water is not great: one volume of water at 20°C dissolves 0.88 volume of CO_2 , and at 0°C —1.7 volumes. Carbon dioxide is used in preparing soda according to the Solvay process (see p. 111), for the synthesis of carbamide (p. 112), for the preparation of salts of carbonic acid, and also for the aeration of soft, mineral, and other beverages.

Carbon dioxide transforms into a liquid at room temperature under a pressure of about 0.6 MPa. Liquid carbon dioxide is stored in steel cylinders. When it is rapidly poured out of a cylinder, much heat is absorbed owing to evaporation so that the CO_2 transforms into a white snow-like substance that sublimates without melting at -78.5°C . Solid carbon dioxide under the name of "dry ice" is used to store perishable food products, in the production and storage of ice-cream, and also in many other cases when a low temperature is needed.

A solution of CO_2 in water has a slightly sour taste and a weakly acidic reaction due to the presence in the solution of a small amount

of carbonic acid H_2CO_3 formed as a result of the reversible reaction:



Consequently, carbon dioxide is the anhydride of carbonic acid.

Equilibrium of the above reaction is greatly shifted to the left—only a very small amount of the dissolved CO_2 transforms into carbonic acid.

Carbonic acid H_2CO_3 can exist only in an aqueous solution. When the latter is heated, carbon dioxide evaporates, the equilibrium of formation of H_2CO_3 shifts to the left, and in the long run pure water remains.

Carbonic acid is very weak. In a solution, it dissociates mainly into H^+ and HCO_3^- ions and forms only a negligible amount of CO_3^{2-} ions:



The dissociation constant of carbonic acid according to the first step, which takes into account the equilibrium of the ions with the entire amount of carbon dioxide in the solution (both in the form of CO_2 and in the form of carbonic acid), is expressed by the relationship:

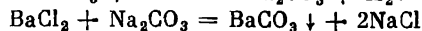
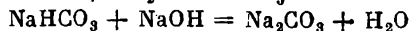
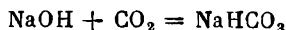
$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2 + \text{H}_2\text{CO}_3]} = 4.5 \times 10^{-7}$$

The dissociation constant according to the second step is:

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.7 \times 10^{-11}$$

Carbonic acid is dibasic and forms two series of salts—normal and acid. The normal salts are called **carbonates**, and the acid ones **hydrogen carbonates** (or **acid carbonates** or **bicarbonates**).

The salts of carbonic acid can be obtained either by reacting carbon dioxide with the relevant alkali, or by means of exchange reactions between the soluble salts of carbonic acid and salts of other acids. For example:

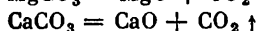


Carbonic acid when reacting with weak bases produces only basic salts in the majority of cases, an example of which is copper carbonate hydroxide $(\text{CuOH})_2\text{CO}_3$. The mineral of this composition encountered in nature is known as **malachite**.

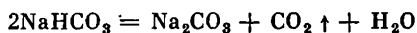
When reacted with even such weak acids as acetic acid, all carbonates decompose with the liberation of carbon dioxide. This reaction is often used to detect carbonates because the liberation of CO_2 is easily discovered by the characteristic hissing sound.

All the carbonates except those of the alkali metals decompose with the liberation of CO_2 when heated. The decomposition products

are generally oxides of the relevant metals, for instance:



Alkali metal hydrogen carbonates transform into the carbonates when heated:

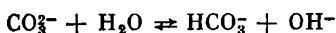


Most hydrogen carbonates, and also potassium, sodium, rubidium, cesium, and ammonium carbonates are soluble in water. The carbonates of the other metals are insoluble.

Solutions of alkali metal carbonates because of hydrolysis have a strongly alkaline reaction:

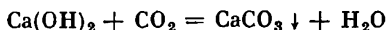


or

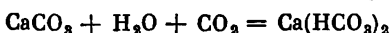


An exceedingly abundant salt of carbonic acid in nature is calcium carbonate CaCO_3 . It occurs as limestone, chalk, and marble.

Calcium carbonate does not dissolve in water. This is why lime water (a solution of calcium hydroxide) becomes turbid when carbon dioxide is passed through it:



If CO_2 is passed through lime water for a long time, however, the initially turbid liquid gradually becomes clarified and, finally, becomes absolutely transparent. Dissolution occurs because of the formation of the acid salt—calcium hydrogen carbonate:



Calcium hydrogen carbonate is an unstable substance. When its solution is boiled or is left to stand for a long time in air, the hydrogen carbonate decomposes with the liberation of CO_2 and the formation of the normal salt.

The solubility of hydrogen carbonates in water explains the constant migration of carbonates in nature. The soil and ground water containing CO_2 seeps through the soil and especially through strata of limestone, dissolves the calcium carbonate and carries it along in the form of the hydrogen carbonate into streams, rivers, and oceans. Thence it gets into the organisms of sea animals and goes to build up their skeletons or, liberating carbon dioxide, again transforms into calcium carbonate and is deposited in stratified form.

In addition to calcium carbonate, another carbonate encountered in nature in large amounts is magnesium carbonate MgCO_3 , known as *magnesite*. Magnesium carbonate, like calcium carbonate, readily dissolves in water containing CO_2 and transforms into the soluble hydrogen carbonate.

Some carbonates are valuable ores and are used for the production of metals (for example, chalybite or spathic iron FeCO_3 , smithsonite ZnCO_3).

Sodium Carbonate (Soda) Na_2CO_3 . In the form of a crystal hydrate, soda corresponds to the formula $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. But this crystal hydrate readily erodes—it loses part of its water of crystallization.

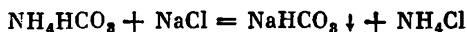
Soda is one of the chief products of the basic chemical industry. It is used in large amounts by the glass, soap, pulp and paper, textile, petroleum, and other branches of industry, and also goes to prepare various salts of sodium. It also finds domestic use, mainly as a detergent.

At present, soda is produced commercially by the **Solvay process** based on the formation of sodium hydrogen carbonate when sodium chloride reacts with ammonium hydrogen carbonate in an aqueous solution.

A concentrated sodium chloride solution is saturated with ammonia, and then carbon dioxide obtained by the calcination of limestone is passed into it under pressure. Reaction of the ammonia with carbon dioxide and water yields ammonium hydrogen carbonate:



The latter enters into an exchange reaction with the sodium chloride to form ammonium chloride and sodium hydrogen carbonate:



The sodium hydrogen carbonate has a comparatively low solubility in cold water, precipitates, and is filtered off.

When sodium hydrogen carbonate is calcined, it decomposes into the carbonate, water, and carbon dioxide, which is recycled:



The ammonia is recovered by heating the solution containing the ammonium chloride with slaked lime:



It is also recycled.

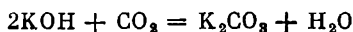
Thus, the only residue of the process is calcium chloride that remains in the solution after the liberation of the ammonia and has a limited application.

Sodium carbonate prepared by the Solvay process contains no water of crystallization and is called **soda ash**.

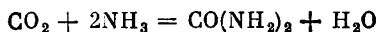
A part of the sodium hydrogen carbonate is used without any further processing. It is employed in medicine under the name **bicarbonate of soda**, and in the baking of bread and in the food industry under the name **baking soda**.

The production of soda ash in the USSR is continuously growing. In 1957, it was 1.6 million tonnes, which is about triple the amount produced in 1940, and in 1976 it reached 4.8 million tonnes.

Potassium carbonate, or **potash**, K_2CO_3 is a white powder that is deliquescent in humid air and well soluble in water. It is employed for the production of soap, in the fabrication of refractory glass, and in photography. Potash is prepared by reacting carbon dioxide with a solution of potassium hydroxide. The latter is obtained in the electrolysis of a potassium chloride solution:



An important compound—**carbamide**, or **urea**, $CO(NH_2)_2$ is produced by reacting carbon dioxide with ammonia under pressure:



This method of producing carbamide was discovered in 1870 by A. Bazarov.

Carbamide is a white crystalline substance well soluble in water. It is used in agriculture as a highly concentrated nitrogen fertilizer, and in farming as an addition to the fodder of ruminants. Carbamide is used to manufacture cheap plastics called **carbamide plastics**. It is also the starting compound for the preparation of many organic substances and medicines. Some carbamide derivatives have herbicidal properties—they are used to combat weeds.

42. Carbon Monoxide

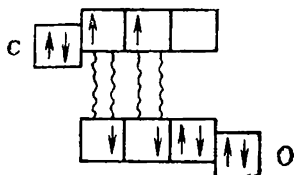
Carbon monoxide CO is a colourless poisonous gas that condenses into a liquid only at -192°C and freezes at -205°C . Carbon monoxide dissolves very poorly in water and does not react with it chemically.

The electron structure of the CO molecule was discussed in Vol. 1, p. 157. As shown in Fig. 53 of Vol. 1, the six valence electrons of the carbon and oxygen atoms occupy three bonding molecular orbitals, forming a triple bond of high strength (1076 kJ/mol).

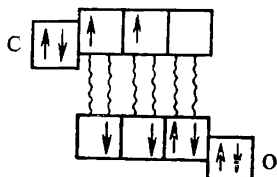
The formation of the triple bond in the CO molecule can also be explained by the method of valence bonds. At the expense of the two unpaired electrons in each of the interacting atoms



two covalent bonds appear:



This diagram shows that one of the orbitals of the outer electron layer of the carbon atom remains unoccupied by electrons, so that this atom can be an acceptor of an electron pair. The oxygen atom, however, retains an unshared electron pair on one of the p orbitals and, consequently, has electron donor properties. The result is the formation of still another covalent bond—a donor-acceptor one:

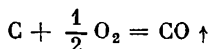


In the molecule thus formed, each atom has eight electrons in its outer layer. The structure of the CO molecule can be depicted by the formula:

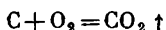


The arrow here shows the donor-acceptor bond.

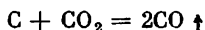
The reaction of formation of carbon monoxide from the elementary substances is described by the equation:



The standard Gibbs energy of this reaction is -137 kJ/mol , but the standard Gibbs energy of the reaction



is much more negative (-394 kJ/mol). This is why at moderate temperatures carbon (coal) burns with the formation of CO_2 , while virtually no carbon monoxide, even with insufficient oxygen, is formed. Matters are different upon elevation of the temperature. When from 400 to 500°C is reached, a reaction begins between the carbon and the carbon dioxide formed:



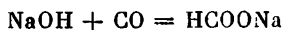
This reaction is endothermic, and at 298 K the change in the standard Gibbs energy is positive (+120 kJ/mol). In the course of combination, however, the number of gas molecules doubles, and the entropy of the system grows very greatly. Hence, the entropy component of the Gibbs energy is negative. With elevation of the temperature, this addend begins to predominate (in absolute value) over the enthalpy term, and as a result the change in the Gibbs energy becomes negative when the reaction proceeds. Already at 800 °C, the degree of conversion of CO₂ to CO reaches 80%.

The above reaction between carbon and CO₂ resulting in the formation of carbon monoxide is conducted on a very large scale in the blast-furnace process (see Sec. 125), and also in gas producers (see Sec. 45).

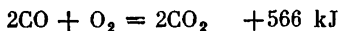
Carbon monoxide is generally prepared in laboratories by adding formic acid HCOOH to heated sulphuric acid. The latter removes water from the formic acid, liberating carbon monoxide:



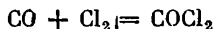
This reaction shows that carbon monoxide can be considered as the anhydride of formic acid. Although formic acid cannot be prepared directly from carbon monoxide and water, its salts are formed when alkali metal hydroxides react with carbon monoxide at 150-200 °C:



Carbon monoxide burns in air with a bluish flame with the evolution of a great amount of heat, transforming into CO₂:



In sunlight or in the presence of activated carbon (a catalyst), carbon monoxide combines directly with chlorine, forming an exceedingly poisonous gas called **phosgene**:

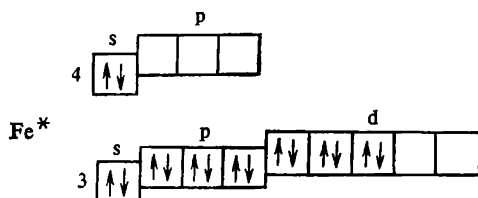


Phosgene is an important industrial product. It is employed in the production of a number of organic and inorganic substances, for instance, dyes.

Carbon monoxide combines with many metals forming **metal carbonyls**, for example iron pentacarbonyl Fe(CO)₅ and nickel tetracarbonyl Ni(CO)₄. The latter two substances are volatile, very poisonous liquids. Most metal carbonyls are crystalline substances. Of the greatest practical significance are the carbonyls of nickel, cobalt, and iron. They are used to prepare highly pure metals (see Sec. 79), and for the application of metal coatings. They are also catalysts of many important chemical reactions.

The chemical bonds in the molecules of metal carbonyls are formed according to the donor-acceptor method at the expense of the

unpaired electron pairs of the CO molecule and the free orbitals of the excited metal atom. For example, an excited iron atom has five unoccupied orbitals:



This is why the iron carbonyl molecule has a composition corresponding to the formula $\text{Fe}(\text{CO})_5$.

At an elevated temperature, carbon monoxide is a good reducing agent that plays an important role in metallurgy in reducing metals from their oxides (see Secs. 78 and 125). It is also used as a gaseous fuel (see Sec. 45) and is one of the reactants in the production of a number of organic compounds.

Carbon monoxide is very poisonous and is especially dangerous because it has no odour (poisoning may occur without being noticed). The explanation of the poisonous action of carbon monoxide is that CO readily combines with the hemoglobin of the blood and renders it incapable of transferring oxygen from the lungs to the tissues. When fresh air is inhaled, the compound formed (carboxy-hemoglobin) gradually decomposes, and the hemoglobin restores its ability to absorb oxygen.

43. Compounds of Carbon with Sulphur and Nitrogen

Of great practical importance among the compounds of carbon with sulphur and nitrogen are carbon disulphide CS_2 and hydrogen cyanide HCN.

Carbon disulphide CS_2 is prepared by passing sulphur vapour through a layer of red-hot coal. It is a colourless volatile liquid with a high refraction index boiling at 46°C . When stored for a long time, carbon disulphide turns yellow and acquires an unpleasant odour.

Carbon disulphide is poisonous and readily ignites. It is a good solvent of sulphur, phosphorus, iodine, various fats, and resinous substances. It is used for combatting plant pests and in the production of rayon (p. 166).

Hydrogen Cyanide HCN. At a high temperature, for instance in an electric arc, carbon can combine directly with nitrogen to form the colourless poisonous gas **dicyanogen** whose molecular mass corresponds to the formula C_2N_2 . In its chemical properties, dicyanogen resem-

bles the halogens somewhat. Like them, with hydrogen it forms the compound HCN having acid properties and known as **hydrogen cyanide** (or **hydrocyanic acid**).

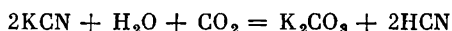
Hydrogen cyanide is a colourless, very volatile liquid boiling at 26.7°C and having the characteristic odour of bitter almond.

In an aqueous solution, hydrogen cyanide dissociates only insignificantly into ions ($K = 8 \times 10^{-10}$).

Hydrogen cyanide is a strong poison that is fatal even in negligible doses (less than 0.05 g).

The salts of hydrogen cyanide are called **cyanides**. Of these salts, potassium cyanide has the greatest application.

Potassium cyanide KCN forms colourless crystals that dissolve well in water. Potassium cyanide is as poisonous as hydrogen cyanide. In the air, under the action of CO_2 , it decomposes quite rapidly, liberating hydrogen cyanide and transforming into the carbonate:



Being a salt of a very weak acid, potassium cyanide becomes greatly hydrolyzed in water:



This is why a solution of potassium cyanide has an alkaline reaction and a strong odour of hydrogen cyanide. Sodium cyanide has similar properties.

Potassium and sodium cyanides are capable of dissolving gold and silver in the presence of the oxygen of the air. This underlies their use for extracting these metals from their ores (see Sec. 88). They are also employed in organic synthesis and in galvanic gold and silver plating.

44. Fuel and Its Kinds

Petroleum, natural gas, coal, and also many carbon compounds play an important role in modern life as energy sources. The combustion of coal and carbon-containing compounds yields heat that is used for production processes, heating, and preparing food. The major part of the heat obtained is converted into other kinds of energy and goes to perform mechanical work.

The main kinds of fuel include mineral or fossil coal, generally called simply coal, peat, wood, petroleum, and natural gas.

Coal is burned directly or processed into more valuable kinds of fuel—coke, liquid and gaseous fuel.

In tsarist Russia, the amount of coal mined could not cover the requirements of even the poorly developed industry, and coal was imported. The only local supplier of coal for the entire country at that time was the Donets Basin.

After the October Revolution, tremendous changes occurred in the coal mining industry. New coal basins were placed into operation in Central Asia, the Caucasus, and in Eastern Siberia. The mining of coal was also commenced in a number of other regions of the country. In 1940, the coal output in the Soviet Union was 166 million tonnes, in 1954 it was 347 million, and in 1977—722 million tonnes. The fraction of coal in the total production of fuel, however, is constantly diminishing because of the growth in the fraction of petroleum and natural gas.

Coal consists of the metamorphosed remains of ancient vegetation. The older the coal, the richer it is in carbon.

Three main kinds of coals are distinguished.

Anthracite, or hard coal, is the oldest coal. It is distinguished by its high density and glance (this is why it is sometimes referred to as glance or glossy coal). Its average carbon content is 95%. It forms about 5.5% of the total coal resources in the USSR.

Bituminous, or soft coal, contains from 75 to 90% of carbon. It is the most widely used of all coals.

Lignite, or brown coal, contains from 65 to 70% of carbon. It has a brown colour. Being the youngest of all coals, it often retains traces of the structure of the tree from which it formed. Brown coal is highly hygroscopic and has a great ash content (from 7 to 38%), and for this reason it is used only as a local fuel and as a starting material for chemical processing (valuable kinds of liquid fuel—petrol and kerosene—are produced by its hydrogenation, p. 14).

Peat is the product of the first stage of coal formation. It is deposited at the bottom of bogs from the dying parts of bog lichens. The USSR is the richest country in the world as regards its explored peat deposits. The carbon content in peat is 55 to 60%. The main drawback of peat as a fuel is its high ash content. It is used as a local fuel.

The dry distillation of peat yields some valuable chemical products, and also **peat coke**. The latter contains very little sulphur, which allows it to be used for smelting high-quality iron.

Wood (firewood) occupies a secondary place in the overall fuel balance. During recent years, its use in industry has been continuously diminishing.

Petroleum found widespread use as a fuel since the internal-combustion engine, running on petroleum-refining products, was invented at the end of the 19th century.

But petroleum is not only a convenient and highly calorific fuel. It is also an important starting material for the production of the most diverse chemical products (synthetic alcohols, detergents, rubber-like materials, solvents, etc.). Casing-head and refinery gases are also widely used as a starting material for the chemical industry. The production of petroleum is constantly growing in the USSR:

Year	1913	1940	1954	1977
Output, million tonnes	10.3	31.1	59.3	546

Natural gas, consisting of methane and other saturated hydrocarbons, is a very cheap and convenient fuel. The importance of natural gas is evident from the fact that during the 25 years from 1937 to 1962 its production in the capitalist countries increased almost six times.

The use of natural gas in the USSR began on an appreciable scale only after the second world war. Major deposits of natural gas were discovered in the Ukrainian SSR, the Krasnodar Region, Central Asia, and in a number of regions in Siberia. At present, many gas pipelines have been laid having a great length. They join the sources of natural gas production to the regions of the industrial and domestic use.

The gas industry belongs to the most rapidly developing branches of our heavy industry. The rates of its growth are characterized by the production of natural gas and of gas obtained by the processing of coal and shale. The total gas production in the USSR is shown by the following figures:

Year	1913	1940	1955	1977
Output, thousand million m ³	0.02	3.4	10.4	346

Natural gas is an excellent fuel; it is also an exceedingly valuable and economically profitable raw material for the organic synthesis industry. A number of new chemical enterprises have been erected in the USSR based on natural gas; quite a few existing enterprises are also being converted to this kind of raw material.

Identical amounts of fuel produce different amounts of heat when burnt. Consequently, to assess the quality of a fuel, its **heating value** is determined, which is the amount of heat liberated in the complete combustion of one kilogram of fuel.

Approximate heating values (in kJ/kg) for various kinds of fuel are given below:

Dry wood	19 000	Anthracite	34 000
Dry peat	23 000	Charcoal	34 000
Brown coal	28 000	Petroleum	44 000
Bituminous coal	35 000	Natural gas	50 000

45. Gaseous Fuel

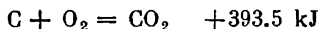
All kinds of solid fuel and petroleum are inferior to natural gas in their heating value. The high heating value of gaseous fuel is due to the fact that unlike solid kinds of fuel or the large molecules of petroleum hydrocarbons, no energy is spent to break the bonds between

the carbon atoms. In addition, gaseous fuel mixes completely with air, so that only a very small excess amount of oxygen in comparison with the theoretical value is needed for its combustion. This lowers the heat losses for heating the excess oxygen (air). A gas can be heated preliminarily, owing to which the temperature of the flame is increased. It can be conveniently transported over great distances with the aid of gas pipelines.

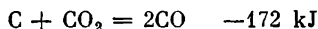
The most important kinds of gaseous fuel include natural gas (see Sec. 44), producer gas, and coke gas.

Producer gas is prepared from solid fuel by the partial oxidation of the carbon that it contains at a high temperature. This process is called gasification of solid fuel. It is carried out in special equipment—gas producers, consisting of a vertical shaft into which fuel is charged from the top, while air, oxygen, steam, or a mixture of these substances is blown in from the bottom. Depending on the composition of the gases blown in, there are distinguished straight, water, mixed, and other producer gases.

Straight gas is obtained when air is blown in. In the bottom part of the producer, the following reaction occurs:

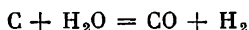


Owing to the large amount of heat thus liberated, the temperature reaches 1400 to 1600 °C, the higher layers of coal become heated, and the coal reacts with the CO_2 :



The gas produced consists chiefly of carbon monoxide and nitrogen.

Mixed (complex) gas is obtained when a mixture of air and steam is blown in. Simultaneously with the above reactions, the carbon reacts with the steam:



Thus, the composition of the mixed gas, in addition to carbon monoxide and nitrogen, includes hydrogen, which increases its heating value. Mixed gas is used in industry as a fuel. It is the most widespread and cheap of all the artificial combustible gases.

Water gas is obtained when steam is fed onto red-hot coal. The gas contains up to 86% of CO and H_2 and is used not as a fuel, but for the synthesis of chemical products.

Coke gas is the name given to the gas produced by heating bituminous coal to 900-1100 °C without the access of air. This gas in the pure state or in a mixture with natural gas is used as a fuel for heating open-hearth furnaces, furnaces in the glass and ceramic industry, and also in municipal facilities. Coke gas is also a starting material in the synthesis of chemical products.

Coke gas is a mixture of various combustible gases. Its composition depends on the starting material, but on an average is expressed by

the following figures (in per cent by volume):

Hydrogen	59
Methane	25
Other hydrocarbons	3
Carbon monoxide	6
Useless admixtures (CO_2 , N_2 , O_2)	7

Underground Gasification of Coal. Coal can be converted into a gaseous fuel by gasifying it directly at the place where it is deposited (underground). The first to advance the idea of such a process was D. Mendeleev in 1888.

At present, work on the underground gasification of coals and combustible shales is in hand in the USSR and a number of foreign countries.

ORGANIC COMPOUNDS

46. General

Carbon compounds (except for a few of the simplest ones) have long been referred to as **organic compounds** because in nature they are encountered almost exclusively in the organisms of animals and plants, participate in vital processes, or are products of the vital activities or decay of organisms. Unlike organic compounds, substances such as sand, clay, various minerals, water, carbon monoxide and dioxide, carbonic acid, its salts, and other salts encountered in "inanimate" nature are called **inorganic** or **mineral substances**.

The division of substances into organic and inorganic ones was the result of the nature of organic compounds, which have specific properties. It was considered for a long time that it is impossible in principle to obtain the carbon-containing substances formed in organisms by synthesis from inorganic compounds.

The formation of organic substances was attributed to the influence of a special incognizable "vital force" acting only in living organisms and underlying the specific nature of organic substances. This theory, which was a variety of the idealistic notions of nature, was named **vitalism** (from the Latin *vis vitalis*—vital force). The vitalists attempted to find in the phenomena of animate nature a proof of the existence of certain mysterious forces in the world that do not lend themselves to investigation and do not obey the general physicochemical laws. The conception of the vitalists was formulated the most completely by one of the most authoritative chemists of the first half of the 19th century—the Swedish scientist J. Berzelius. The vitalistic viewpoints hindered progress in the studying of the nature of organic substances and were refuted in the course of development of science.

In 1824, the German chemist F. Wöhler, a pupil of Berzelius, for the first time in history produced oxalic acid $\text{HOOC}-\text{COOH}$, an organic compound that up to that time was produced only from plants, from the inorganic substance dicyanogen $\text{NC}-\text{CN}$ by heating it with water. In 1828, Wöhler synthesized a substance of an animal origin for the first time: by heating the inorganic compound ammonium cyanate NH_4CNO , he obtained urea (carbamide) $(\text{NH}_2)_2\text{CO}$; previously this substance was obtained only from urine.

Soon other organic substances were synthesized in laboratory conditions: in 1845 in Germany, H. Kolbe synthesized acetic acid, in 1854 in France, M. Berthelot prepared a fat synthetically, in 1861 A. Butlerov in Russia synthesized a saccharide substance, and so on.

At present, many organic compounds are synthesized. Moreover, it was found much simpler and cheaper to produce many organic substances synthetically than to separate them from natural substances. The greatest success of chemistry in the fifties and sixties of the 20th century was the first synthesis of simple proteins—the hormone insulin and the enzyme* ribonuclease. This proved the possibility of preparing synthetically even proteins—the most complex organic substances that are participants without fail of all vital processes; according to the definition of F. Engels: "Life is a way of existence of protein bodies".

With the development of the synthesis of organic compounds, the distinction between these compounds and inorganic ones was destroyed, but the name "organic compounds" remained. Most carbon compounds known at present are not even encountered in organisms, but have been prepared artificially.

47. Features of Organic Compounds

We have already indicated that the number of carbon compounds studied to date is exceedingly great. But notwithstanding the diversity of the natural organic substances, they generally consist of a small number of elements. In addition to carbon, they almost always include hydrogen, frequently oxygen and nitrogen, and sometimes sulphur and phosphorus. These elements were called **organo-gens** (i.e. elements giving birth to organic molecules)**.

The phenomenon of **isomerism** (p. 130) is especially widespread among organic compounds. There are numerous carbon compounds

* **Hormones** are substances produced by the internal secretion glands—regulators of the most important functions of the organism of human beings and animals (for instance, insulin is a hormone of the pancreas—a regulator of sugar exchange). For **enzymes**, see Vol. 1, p. 190.

** With the development of chemistry, organic substances containing many other elements were synthesized. Compounds in which metals (Li, Na, K, Mg, Zn, Hg, Al, Sn, Pb, etc.) and certain non-metals (for instance, Si, As) are directly bonded to carbon were called **organo-element compounds**.

having an identical qualitative and quantitative composition and an identical molecular mass, but absolutely different physical and, quite frequently, chemical properties. For example, two different isomeric organic substances have the composition C_2H_6O , and, accordingly, the molecular mass 46.07. They are ethyl alcohol—a liquid boiling at $78.4^\circ C$ and miscible with water in any proportions, and dimethyl ether—a gas that is virtually insoluble in water and differs noticeably from ethyl alcohol in its chemical properties (see also p. 131).

Isomerism, particularly, is a reason why there is such a great diversity of organic substances.

Unlike mineral substances, organic ones behave specifically when heated. Their melting point does not exceed 350 to $400^\circ C$, while in the majority of cases they melt below 200 – $100^\circ C$. When heated without the access of air, organic substances can undergo deep changes as a result of which new substances are formed having absolutely different properties, or (at temperatures of the order of 400 – $600^\circ C$) they can undergo complete decomposition and charring. If heating is conducted in the presence of the oxygen of the air or other oxidizing agents, organic substances usually burn to the end*; the carbon and hydrogen in them are completely transformed into carbon dioxide and water, while the nitrogen is generally liberated in the free state**.

One of the most important features of organic compounds making an imprint on all their chemical properties is the nature of the bonds between the atoms in their molecules. The overwhelming majority of these bonds have a strikingly expressed covalent nature. This is why organic substances are mainly non-electrolytes, do not ionize in solution, and comparatively slowly react with one another. The time needed for the completion of reactions between organic substances is usually measured in hours, and sometimes in days. For this reason, various catalysts in organic chemistry are highly important.

Finally, it is necessary to stress once more the exclusive biological role of organic compounds. Many of them are direct carriers, participants, or products of processes occurring in living organisms, or, like enzymes, hormones, vitamins and the like, are biological catalysts, initiators, and regulators of these processes.

* Valuable organic substances distinguished by their exclusive stability to the action of oxidizing agents and high temperatures have been prepared only synthetically. They include perfluorocarbons (perfluoroparaffins or perfluoroalkanes) and fluoroplastics (p. 172).

** This underlies the quantitative analysis of organic substances: the content of carbon and hydrogen in a burned substance is determined according to the amount of CO_2 and H_2O formed, the volume of the liberated N_2 is measured directly according to its volume, while the oxygen content is established according to the difference between the mass of the burned substance and that of the other elements contained in it.

48. The Theory of the Chemical Structure of Organic Compounds

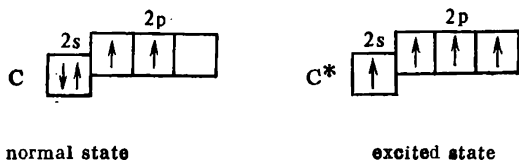
The chemical nature of organic compounds, the properties distinguishing them from inorganic compounds, and also their diversity were explained in the theory of chemical structure (see Vol. 1, Sec. 38) formulated by Butlerov in 1861.

According to this theory, the properties of compounds are determined by their qualitative and quantitative composition, their chemical structure, i.e. the sequence of combination with one another of the atoms forming a molecule, and their mutual influence. The theory of the structure of organic compounds, developed and supplemented by the latest ideas in the field of the chemistry and physics of atoms and molecules, especially by the notions of the spatial structure of molecules, the nature of chemical bonds, and the nature of the mutual influence of atoms, forms the theoretical foundation of organic chemistry*.

The following principles are the basic ones in the modern theory of the structure of organic compounds.

1. All the features of organic compounds are determined first of all by the properties of the element carbon.

In accordance with the position carbon occupies in the periodic table, the outer electron layer of its atom (the *L* shell) has four electrons. It does not exhibit a clearly expressed inclination to give up or attach electrons, and in this respect it occupies an intermediate position between metals and non-metals. It is characterized by a sharply expressed ability to form covalent bonds. The structure of the outer electron layer of the carbon atom can be pictured as follows:

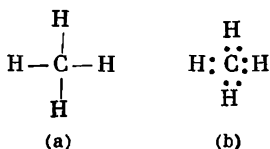


An excited carbon atom can participate in the formation of four covalent bonds. Consequently, in the overwhelming majority of its compounds, carbon displays a valence equal to four.

For instance, the simplest organic compound—the hydrocarbon methane—has the composition CH_4 . Its structure can be depicted

* Butlerov's teaching on the mutual influence of atoms was developed in greater detail by his pupil V. V. Markovnikov (1838-1904), a professor at the Moscow University, and also by many other of his pupils and followers both in this country and abroad. The study of the mutual influence of atoms is one of the most important problems in the modern chemistry of organic compounds.

by the following structural (a) or electron dot (b) formulas:



The electron dot formula shows that the carbon atom in the methane molecule has a stable eight-electron outer shell (an electron octet), and the hydrogen atoms, a stable two-electron shell (an electron doublet).

All four covalent bonds of carbon in methane (and in other similar compounds) are equivalent and symmetrically directed in space. The carbon atom, as it were, is at the centre of a tetrahedron (a regular tetrahedral pyramid), while the four atoms combined with it (in methane—four hydrogen atoms) are at the corners of the tetrahedron (Fig. 16). The angles between the directions of any pair of bonds (the valence angles of the carbon) are identical and equal $109^{\circ}28'$.

The explanation is that in the carbon atom, when it forms covalent bonds with four other atoms, four hybrid sp^3 orbitals symmetrically arranged in space and extended in the direction towards

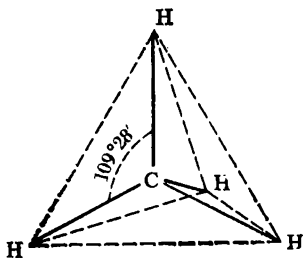


Fig. 16. Tetrahedral model of a methane molecule

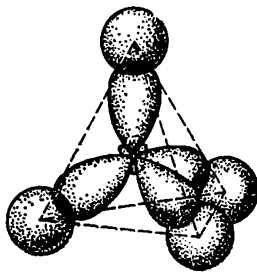


Fig. 17. Formation of sigma bonds in a methane molecule

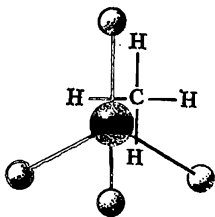


Fig. 18. Spherical model of a methane molecule

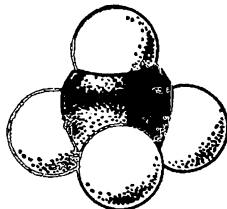


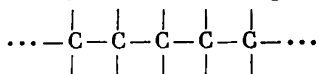
Fig. 19. Segment model of a methane molecule

the tetrahedron corners are formed from one s and three p orbitals as a result of sp^3 hybridization.

Overlapping of the sp^3 hybrid electron clouds of the carbon with the electron clouds of the other atom (in methane with the spherical clouds of the hydrogen atom $1s$ electrons) causes four tetrahedrally directed covalent sigma bonds to be formed (Fig. 17; see also Vol. 1, Sec. 42).

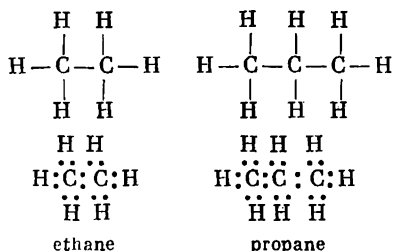
The tetrahedral structure of the methane molecule is clearly shown by its spatial models—a spherical (Fig. 18) or segment (Fig. 19) one. The white spheres (segments) depict the hydrogen atoms, and the black ones, the carbon. The spherical model characterizes only the mutual arrangement of the atoms in space, while the segment one, in addition, gives an idea of the relative interatomic distances (the distances between the atomic nuclei). As shown in Fig. 18, the structural formula of methane can be considered as the projection of its spatial model onto the plane of the drawing.

2. An exclusive property of carbon underlying the diversity of organic compounds is the ability of its atoms to combine with one another by means of stable covalent bonds, forming carbon chains of a virtually unlimited length*:



The valences of the carbon atoms not participating in the mutual bonding are used to attach other atoms or groups (in hydrocarbons for attaching hydrogen).

For example, the hydrocarbons **ethane** (C_2H_6) and **propane** (C_3H_8) contain chains consisting of two and three carbon atoms, respectively. Their structure is shown by the following structural and electron dot formulas:



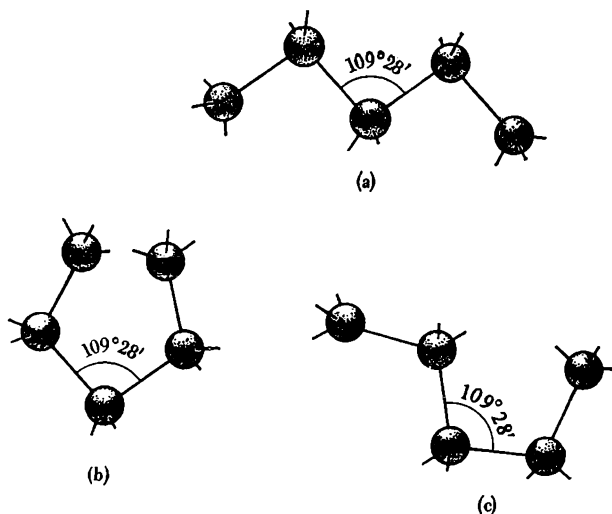
Compounds are known containing hundreds of carbon atoms in the chains and even more.

* Apart from carbon, chains of identical atoms are formed by its analogue from Group IV—silicon. These chains, however, contain not over six Si atoms. Long chains of sulphur atoms are known, but the compounds containing them are not stable.

The growth of a carbon chain by one carbon atom leads to an increase in the composition by a CH_2 group. Such a quantitative change results in a new compound having somewhat other properties, i.e. differing qualitatively from the initial compound; the general nature of the compounds, however, is retained. For instance, in addition to the hydrocarbons methane (CH_4), ethane (C_2H_6), propane (C_3H_8), there also exist **butane** (C_4H_{10}), **pentane** (C_5H_{12}), and so on. Among the enormous diversity of organic substances, consequently, we can separate **series of compounds of a single kind** in which each following member differs from the preceding one by a CH_2 group. Such series are called **homologous**, their members with respect to one another are known as **homologues**, and the existence of such series is called the **phenomenon of homology**.

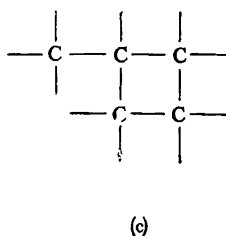
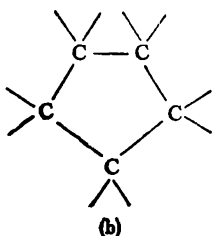
Consequently, the hydrocarbons methane, ethane, propane, etc. are homologues of the same series called the **series of saturated hydrocarbons**, or, according to the name of the first representative—the **methane series**.

Since carbon bonds are directed tetrahedrally, carbon atoms forming a chain are arranged not along a straight line, but in a zigzag fashion, and since the atoms can rotate about the axis of a bond, the chain can take on different conformations:



Such a chain structure allows the terminal (b) or other non-adjacent atoms (c) to approach each other. As a result of the formation of a bond between these atoms, the carbon chains may

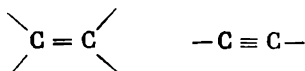
close up into rings, for instance:



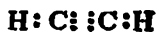
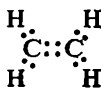
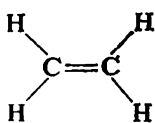
Thus, the diversity of organic compounds is also explained by the circumstance that with an identical number of carbon atoms in a molecule, compounds are possible with an open chain of the carbon atoms, and also compounds whose molecules contain rings (cyclic compounds).

3. The covalent bonds between carbon atoms formed by one pair of shared electrons are called **single bonds**.

A bond between carbon atoms can be formed by two or three shared pairs of electrons instead of one. The result is chains with **multiple—double or triple—bonds**. These bonds can be depicted as follows:



The simplest compounds containing multiple bonds are the hydrocarbons **ethylene** (with a double bond) and **acetylene** (with a triple bond):



ethylene

acetylene

Hydrocarbons with multiple bonds are called **unsaturated**. Ethylene and acetylene are the first representatives of two homologous series—**ethylene hydrocarbons** and **acetylene hydrocarbons**.

The single covalent bond C—C (or C : C) formed by the overlapping of two sp^3 hybrid electron clouds along the line connecting the centres of the atoms (along the bond axis), as, for example, in

ethane (Fig. 20) is a sigma bond (see Vol. 1, p. 139). The C—H bonds are also sigma bonds—they are formed by overlapping of the sp^3 hybrid cloud of the C atom and the spherical cloud of the $1s$ electron of the H atom along the bond axis.

The multiple carbon-carbon bonds have a somewhat different nature. For instance, in an ethylene molecule upon the formation of the double covalent bond $C=C$ (or $C::C$), one s orbital and only two p orbitals in each carbon atom participate in hybridization (sp^2 hybridization), one of the p orbitals of each carbon atom is not hybridized. As a result, three sp^2 hybrid electron clouds are formed that participate in the formation of three sigma bonds. Altogether, an ethylene molecule has five sigma bonds (four C—H and one C—C). They are all arranged in one plane at angles of about 120 degrees with one another (Fig. 21).

Thus, one of the electron pairs in the $C=C$ bond forms a sigma bond, while the second bond is formed by p electrons not participating in hybridization; their clouds retain the shape of dumbbells, are oriented at right angles to the plane in which the sigma bonds are arranged, and overlap above and below this plane (Fig. 22), forming a pi bond (see Vol. 1, p. 139). Hence, the double $C=C$ bond is a combination of one sigma and one pi bond.

The triple bond $C\equiv C$ (or $C:::C$) is a combination of one sigma bond and two pi bonds. For example, in the formation of an acetylene molecule, in each of the carbon atoms, one s orbital and only one p

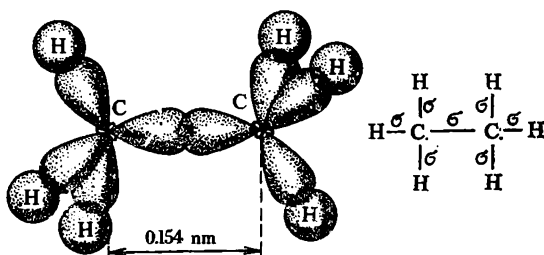


Fig. 20. Formation of sigma bonds in an ethane molecule

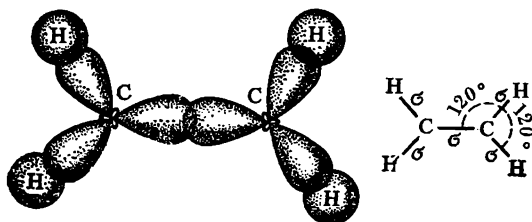


Fig. 21. Formation of sigma bonds in an ethylene molecule

orbital participate in hybridization (*sp* hybridization). The result is the formation of two *sp* hybrid electron clouds participating in the formation of two sigma bonds. The clouds of two *p* electrons of each carbon atom are not hybridized; they retain their configuration and participate in the formation of two *pi* bonds. Acetylene thus contains altogether three sigma bonds (one C—C and two C—H directed along a single straight line) and two *pi* bonds oriented in two mutually perpendicular planes (Fig. 23).

Multiple (i.e. double and triple) bonds readily transform into single ones in reactions; a triple bond first transforms into a double one, and the latter into a single one. This is due to their high reactivity and occurs when atoms are added to a pair of carbon atoms with a multiple bond.

The transition of multiple bonds into single ones is explained by the fact that *pi* bonds usually have a lower strength and, consequently, a greater lability than sigma bonds. When *pi* bonds are formed, the *p* electron clouds with parallel axes overlap to a considerably smaller extent than electron clouds overlapping along the bond axis (i.e. hybrid *s* electron clouds, or *p* electron clouds oriented along the bond axis).

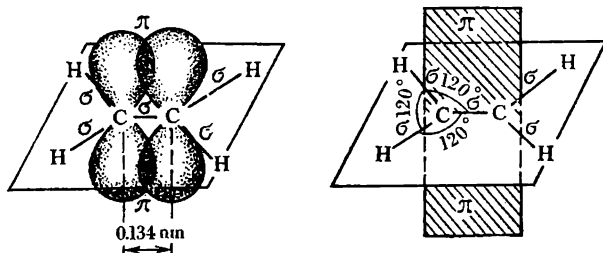


Fig. 22. Formation of a *pi* bond in an ethylene molecule

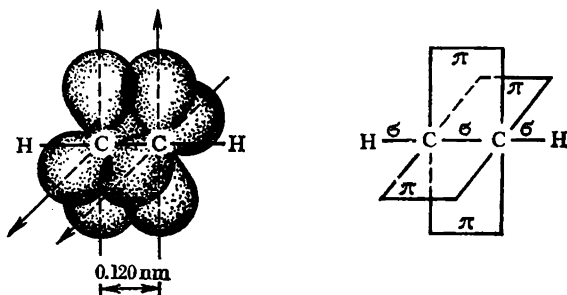


Fig. 23. Formation of *pi* bonds in an acetylene molecule

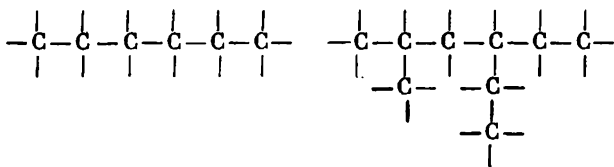
Multiple bonds are stronger than single ones. For instance, the strength of the $\text{C}\equiv\text{C}$ bond is 535 kJ/mol, that of the $\text{C}=\text{C}$ bond is 423 kJ/mol, and of the $\text{C}-\text{C}$ bond only 264 kJ/mol.

It follows from the above that in formulas, two lines of the three in the bond $\text{C}\equiv\text{C}$ and one line of the two in the bond $\text{C}=\text{C}$ signify a bond having a lower strength than the single bond $\text{C}-\text{C}$.

Figures 24 and 25 show spherical and segment spatial models of compounds having a double (ethylene) and a triple (acetylene) bond.

4. The theory of structure explained the numerous cases of isomerism of organic compounds.

Chains of carbon atoms may be unbranched or branched:



For instance, the composition C_5H_{12} corresponds to three saturated hydrocarbons (pentanes) having different chain structures—one with an unbranched chain (normal structure) and two with a branched

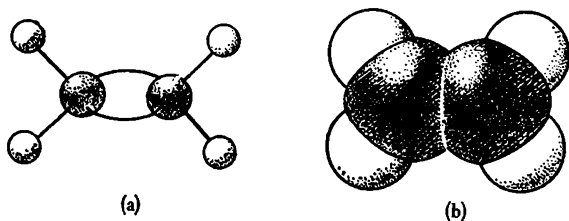


Fig. 24. Models of an ethylene molecule:
a—spherical; b—segment

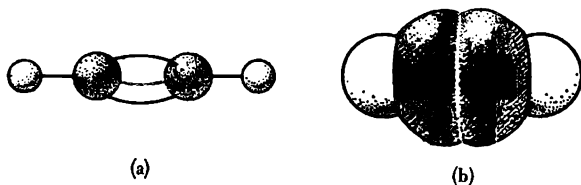
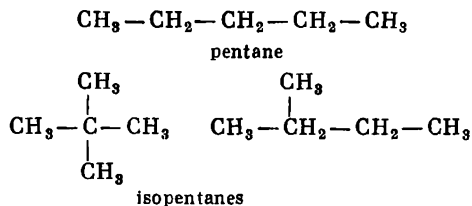
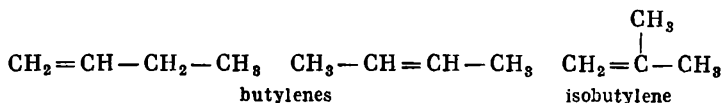


Fig. 25. Models of an acetylene molecule:
a—spherical; b—segment

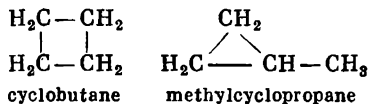
structure (isostructure):



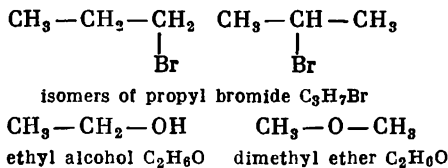
The composition C_4H_8 corresponds to three unsaturated hydrocarbons (butylenes)—two with a normal structure but isomeric with respect to the position of the double bond, and one having an isostructure:



Two cyclic hydrocarbons also having the composition C_4H_8 and isomeric to each other with respect to the ring size are isomers of the above alkenes. They are



While having the same composition, compounds may differ in their structure owing to a different position of atoms other than carbon in the carbon chain, for example:



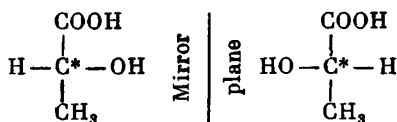
Isomerism may be due not only to different order in the joining of the atoms. Several kinds of **spatial isomerism** or **stereoisomerism** are known, consisting in that with an identical composition and order in the joining of the atoms, the relevant isomers (stereoisomers) differ in the arrangement of the atoms (or groups of atoms) in space.

For example, if a compound has a carbon atom bonded to four different atoms or groups of atoms (an **asymmetrical atom***), then

* The presence of such an atom leads to asymmetry of the molecules. It is evident that both models in Fig. 26 are asymmetrical—a plane of symmetry cannot be drawn through either of them.

two stereoisomeric forms of such a compound are possible. Figure 26 shows two tetrahedral models of lactic acid $\text{CH}_3-\overset{*}{\text{CH}}-\text{COOH}$ in

which the asymmetrical carbon atom (indicated by an asterisk in the formula) is at the centre of the tetrahedron. It is not difficult to see that these models cannot be superimposed in space: they are mirror images and show the spatial configuration of molecules of two different substances (in the given example of lactic acids) differing in certain physical, and chiefly in biological properties. Such isomerism can be referred to as **mirror stereoisomerism**, and the relevant isomers are called **enantiomers***. The difference in the spatial structure of enantiomers can also be represented by structural formulas in which the different arrangement of atomic groups with an asymmetric atom is shown. For instance, for the enantiomers of lactic acid shown in Fig. 26, we have:



We have already mentioned that carbon atoms joined by a double bond are in the same plane as the four bonds joining them to other atoms; the angles between the directions of these bonds are approximately the same (see Fig. 22). When different atoms or groups are joined to each of the carbon atoms with a double bond, **geometric stereoisomerism**, or **cis-trans-isomerism**, is possible. An example is

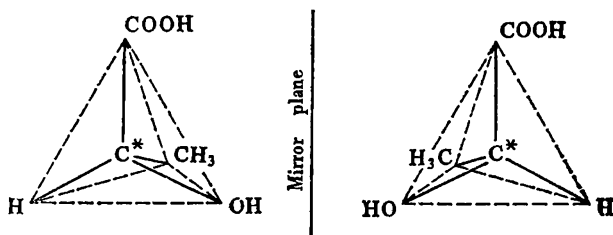
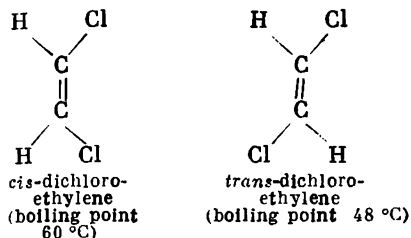


Fig. 26. Tetrahedral models of molecules of lactic acid enantiomers

* Stereoisomers with asymmetrical atoms including enantiomers differ in their optical properties, namely, in their influence on the polarized light passed through them; this is why they are also called **optical isomers** (see a textbook on organic chemistry).

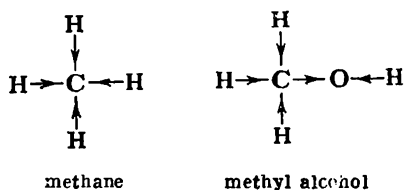
the spatial geometric isomers of dichloroethylene $\text{CHCl}=\text{CHCl}$:



In the molecules of one isomer, the chlorine atoms are at the same side of the double bond, and in those of the other isomer at opposite sides. The former configuration is called a *cis*-, and the latter a *trans*-configuration. Geometric isomers differ from one another in their physical and chemical properties. They exist because the double bond excludes the possibility of free rotation of the atoms it joins about the bond axis (such rotation requires breaking of the pi bond, see Fig. 22).

5. Mutual influence in the molecules of organic substances is exhibited first of all by atoms directly bonded to each other. In this case, the influence is determined by the nature of the chemical bond between them, the magnitude of the difference between their electronegativities, and, consequently, by the degree of polarity of the bond.

For example, if we judge by the summary formulas, all four hydrogen atoms in a methane molecule (CH_4) and a methyl alcohol molecule (CH_4O) should have identical properties. But it will be shown below that one of the hydrogen atoms in methyl alcohol is capable of being substituted by an alkali metal, whereas in methane the hydrogen atoms do not exhibit such an ability. The explanation is that in the alcohol, the hydrogen atom is directly bonded not to the carbon, but to the oxygen:



In the above structural formulas, the arrows on the bond lines conditionally show the displacement of the electron pairs forming a covalent bond owing to the different electronegativity of the atoms. In methane, such a displacement in the bond $\text{H} \rightarrow \text{C}$ is not great

because the electronegativity of carbon (2.5) is only slightly greater than that of hydrogen (2.1) (see Table 6 in Vol. 1, p. 129). Also, the methane molecule is symmetrical. In the alcohol molecule, however, the bond $O \leftarrow H$ is considerably polarized because the oxygen (its electronegativity is 3.5) attracts the electron pair to a much greater extent. For this reason, the hydrogen bonded to the oxygen acquires a greater mobility, i.e. is detached more readily in the form of a proton.

The mutual influence of atoms not bonded directly to one another is also of significance in organic molecules. For instance, in methyl alcohol under the influence of the oxygen, the reactivity not only of the hydrogen atom bonded to the oxygen grows, but also that of the hydrogen atoms not bonded directly to the oxygen, but to the carbon atom. Hence, methyl alcohol is quite readily oxidized, whereas methane is relatively stable to the action of oxidizing agents. The explanation is that the oxygen of the hydroxyl group attracts quite

considerably the pair of electrons in the bond $\overset{\delta+}{C} \rightarrow \overset{\delta-}{O}$ joining it to the carbon whose electronegativity is smaller. As a result, the effective charge (see Vol. 1, p. 130) of the carbon atom becomes more positive. This causes additional displacement of the electron pairs also in the bonds $H \rightarrow C$ in methyl alcohol in comparison with the same bonds in a methane molecule. Under the action of oxidizing agents, the H atoms bonded to the carbon atom that the group OH is bonded to detach themselves considerably more readily than in hydrocarbons and combine with oxygen to form water. The carbon atom bonded to the OH group undergoes further oxidation (p. 155).

The mutual influence of atoms not bonded directly to one another can be transmitted over a considerable distance along the chain of carbon atoms and is explained by the displacement of the electron cloud density in the entire molecule caused by the different electronegativities of its atoms or atomic groups. The mutual influence can also be transmitted through the space surrounding a molecule as a result of overlapping of the electron clouds of close atoms.

49. Classification of Organic Compounds

The following three series are distinguished among organic compounds, depending on the structure of the carbon chains.

Compounds with an open chain of the carbon atoms, also known as acyclic or aliphatic compounds or compounds of the fatty series*. Depending on the nature of the bonds between the carbon atoms, these compounds are divided into saturated ones, containing only single bonds in their molecules, and unsaturated ones whose molecules have multiple (double or triple) bonds between the carbon atoms.

* The last name has a historic origin; the first compounds with long open carbon chains that were studied were acids contained in fats.

Compounds with a closed chain of the carbon atoms, or carbocyclic ones. These compounds, in turn, are subdivided into:

(a) **compounds of the aromatic series**; they are characterized by the presence in their molecules of a special cyclic arrangement of six carbon atoms—the **benzene ring**. This ring is distinguished by the nature of the bonds between the carbon atoms and imparts special chemical properties called **aromatic properties** to the compounds containing it (pp. 146, 148).

(b) **alicyclic compounds**—all the remaining carbocyclic compounds. They are distinguished according to the number of carbon atoms in the ring and, depending on the nature of the bonds between these atoms, may be saturated or unsaturated.

Heterocyclic Compounds. The molecules of these compounds have rings containing **heteroatoms**, i.e. atoms of other elements (oxygen, nitrogen, sulphur, etc.) in addition to the carbon atoms.

The compounds of each of the series indicated above are subdivided into **classes**.

The simplest compounds in the acyclic and carbocyclic series are **hydrocarbons** consisting only of carbon and hydrogen. All the other compounds of these series are considered to be **hydrocarbon derivatives** formed by the replacement of one, two, or several hydrogen atoms in a hydrocarbon molecule by other atoms or groups of atoms*.

The residues of hydrocarbons formed when one, two, or several hydrogen atoms are detached from their molecules are called **hydrocarbon radicals**. Monovalent radicals are designated by the symbol $R\cdot$, divalent ones by the symbol $-R-$ (or $R<$), and trivalent ones by the symbol $-R<$.

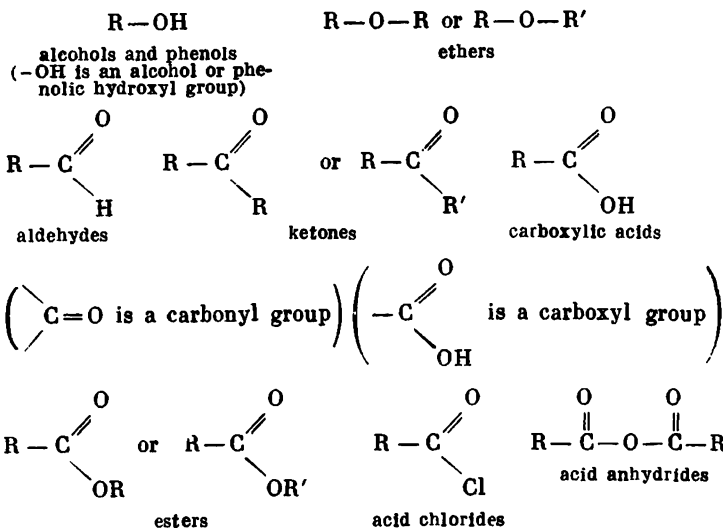
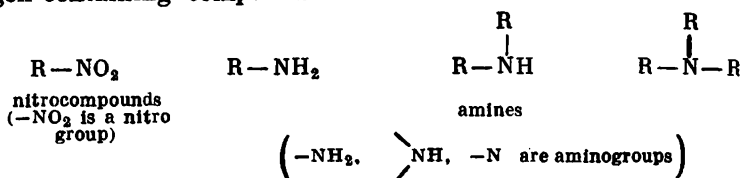
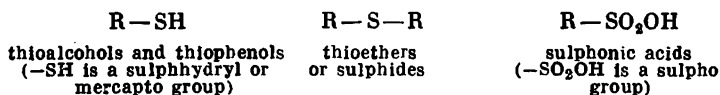
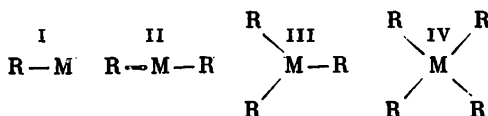
The atoms or groups of atoms replacing hydrogen in a parent hydrocarbon form **functional** or **characteristic** groups** giving rise to the general chemical properties of substances belonging to the same class of hydrocarbon derivatives. Below are given the general formulas and names of some classes of organic compounds (the formulas and names of the functional groups are given in parentheses).

Halogen derivatives of hydrocarbons:

$R-F$	$R-Cl$	$R-Br$	$R-I$
fluoroderivatives	chloroderivatives	bromoderivatives	iododerivatives

* Heterocyclic groupings—five-membered, six-membered, etc.—containing nitrogen, oxygen, sulphur, or other heteroatoms are taken as the basis for the classification in the series of heterocyclic compounds.

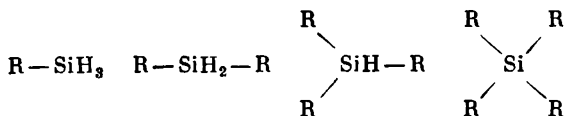
** The term **characteristic groups** has been adopted in the systematic nomenclature of organic compounds being worked out by the International Union of Pure and Applied Chemistry (IUPAC).

Oxygen-containing compounds:**Nitrogen-containing compounds:****Sulphur-containing compounds:****Organoelement compounds:****(a) Organometallic compounds*:**

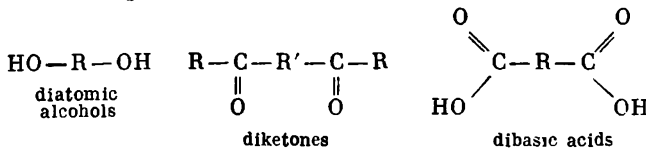
* I II III IV

M, M, M, M are mono-, di-, tri-, and tetravalent metals.

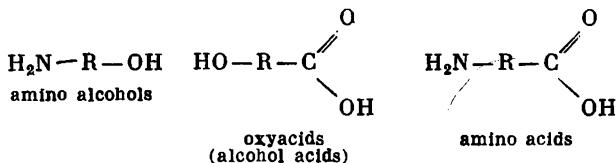
(b) Organosilicon compounds:



Compounds are possible with repeating identical functional groups:



Many organic compounds contain two or more different functional groups (**polyfunctional compounds**). Examples are:



Compounds with different functional groups have a dual nature. For example, amino acids exhibit properties of both amines and acids simultaneously, but both properties are altered somewhat owing to the mutual influence of the functional groups.

The classes of organic substances are very diverse. Below we shall briefly consider only the most important of them.

50. Saturated Hydrocarbons (Alkanes) *

The simplest representative of this class is methane CH_4 . It is a colourless light combustible gas having no odour and almost insoluble in water. Its boiling point is -161.5°C , and its freezing point is -182.5°C .

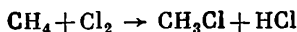
Methane occurs quite frequently in nature. It is the main constituent of **natural gas** deposits (up to 97%), is contained in a considerable amount in **casing head gas** (liberated in the extraction of petroleum), and also in **coke gas**. It is evolved from the bottom of swamps, ponds, and stagnant bodies of water where it is formed as a result of the decomposition of plant remains without the access of air, which is the origin of its name **marsh gas**. Finally, methane

* According to the rules of the IUPAC systematic nomenclature, the saturated hydrocarbons are called **alkanes**. Their old name—**paraffins**—is also encountered quite often. It originates from the Latin words *parum affinitatis*—deprived of affinity—and reflects the exclusive lack of activity of these hydrocarbons in reactions.

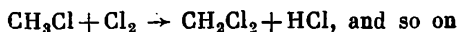
constantly accumulates in coal mines, where it is called **mine gas** or **firedamp**.

A mixture of methane with air is extremely explosive (especially in the proportion 1 : 10).

The methane molecule is quite stable. In ordinary conditions, methane reacts actively (with an explosion) with fluorine, reacts very slowly with chlorine, and does not react almost at all with bromine. The reaction with chlorine or bromine is accelerated by light, and also by heating, and consists in the consecutive **replacement of atoms of hydrogen by halogen atoms** with the formation of **halogen derivatives**, for example:



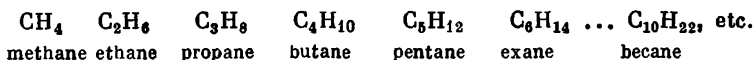
methyl
chloride
(chloro-
methane)



dichloro-
methane

Methane burns with a bluish or almost colourless flame, evolving a great amount of heat (879 kJ/mol). In ordinary conditions, it is not oxidized by a solution of potassium permanganate (the purple colour of the KMnO_4 solution does not vanish upon contact with saturated hydrocarbons).

We have already indicated that methane is the first representative of the homologous series of saturated hydrocarbons or alkanes:



In the molecules of these compounds, all the bonds between the carbon atoms are single ones, and the carbon atoms are "saturated" with hydrogen to the limit. The composition of any of the homologues corresponds to the general formula $\text{C}_n\text{H}_{2n+2}$ (where n is the number of carbon atoms). This regularity allows us to write the formula showing the composition of a saturated hydrocarbon having any number of carbon atoms, for instance, $\text{C}_{18}\text{H}_{38}$ (octadecane) and $\text{C}_{100}\text{H}_{202}$ (hectane).

The composition of the monovalent radicals obtained by detaching a hydrogen atom from a molecule of a saturated hydrocarbon is expressed by the formula $\text{C}_n\text{H}_{2n+1}$ —. Their names are formed by replacing the suffix *-ane* in the name of the hydrocarbon with the suffix *-yl*. For instance, **methyl** CH_3 — is derived from methane, **ethyl** C_2H_5 — from ethane, **propyl** C_3H_7 — from propane, and in general an **alkyl** from an alkane.

As in other homologous series, a general law of nature—the law of the transition of quantitative changes into qualitative ones—manifests itself in the methane series. The change in the composition

of a molecule by the group CH_2 every time results in a new substance which, although having much in common with its neighbours in the series, differs in some properties from them. The difference between homologues is clearly exhibited in their physical properties. The lower members of the saturated hydrocarbon series (from CH_4 to C_4H_{10}) are gases; the middle members (from C_5H_{12} to $\text{C}_{16}\text{H}_{34}$) are liquids at a temperature up to 20°C ; the remaining members in ordinary conditions are solids. In all cases, the boiling and freezing points grow with an increasing molecular mass of the hydrocarbon.

At the same time, the saturated hydrocarbons in a chemical respect are similar to methane. They are very inert, enter only into reactions of hydrogen substitution that proceed very slowly, and do not decolorize solutions of bromine and potassium permanganate when cold.

All the saturated hydrocarbons burn and can be used as fuel. They are contained in petroleum and their distillation products. In **fractional distillation**, petroleum is separated into fractions (distillates) differing in their boiling points, and the following petroleum products are obtained:

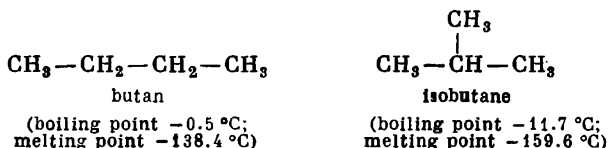
(a) **petrols or gasolines** (boiling point 40 to 180°C) contain hydrocarbons from C_5H_{12} to $\text{C}_{10}\text{H}_{22}$; upon repeated distillation light petroleum products boiling in narrower limits can be separated from them, namely, **petroleum ether** (40 - 70°C), **aviation petrol** (70 - 100°C), and **motor vehicle petrol** (100 - 120°C);

(b) **paraffin oils or kerosenes** (boiling point 180 - 270°C) contain hydrocarbons from $\text{C}_{10}\text{H}_{22}$ to $\text{C}_{16}\text{H}_{34}$;

(c) **solar or gas oils** (boiling point 270 - 360°C) contain mixtures of hydrocarbons from C_{12} to C_{20} ; they are used to prepare lubricating oils and various kinds of diesel fuel;

(d) the **residual material** (petroleum residues up to 40 - 50%) contains still heavier (higher) hydrocarbons; it is used to produce **heavy lubricating oils**, **vaseline (petrolatum)**, and **paraffin wax**.

We have indicated on a previous page that a growth in the number of carbon atoms in molecules is attended by a sharp growth in the number of isomers of the saturated hydrocarbons. Methane CH_4 , ethane C_2H_6 , and propane C_3H_8 have no isomers; there are two butanes C_4H_{10} :



There are three isomeric pentanes C_5H_{12} , five hexanes C_6H_{14} , nine heptanes C_7H_{16} , 18 octanes C_8H_{18} , and 35 nonanes C_9H_{20} . All these hydrocarbons have been obtained. There can be 75 decanes

$C_{10}H_{22}$, and 4347 isomeric hydrocarbons can have the formula $C_{15}H_{32}$. Only some of the isomers are known for the higher homologues, but the possibility in principle of their existence was predicted and proved by Butlerov. He carried out the first synthesis of a hydrocarbon with a branched chain—isobutane.

Both individual homologues and their isomers differ from one another not only in their physical, but also in their chemical properties. Great branching of the carbon chain often results in elevation of the freezing point, and a high content of such hydrocarbons in petrols may limit the possibility of using the latter in cold weather.

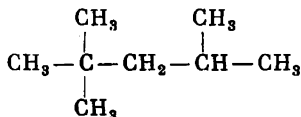
The difference in chemical properties tells, particularly, in the inclination of some of the hydrocarbons in motor vehicle fuel to knock.

The knocking of engine fuel consists in the exceedingly rapid decomposition (explosion) of hydrocarbons that occurs suddenly when the combustible mixture is compressed in an engine cylinder. Knocking does not make it possible to achieve a high compression ratio of the combustible mixture*, and results in the excessive consumption of fuel and rapid wear of the engine. The knocking properties of a fuel depend on the structure of the hydrocarbon chains in the hydrocarbon molecules it is composed of. Isomers having a greatly branched chain knock with much greater difficulty than isomers with an unbranched chain.

The antiknocking properties of engine fuel are characterized by its octane number. The standard substances used for comparison in determining the octane number are the hydrocarbon heptane C_7H_{16} with an unbranched chain of atoms that knocks very readily and one of the isomers of octane (isooctane) having a branched chain of atoms with a low inclination to knocking:



heptane



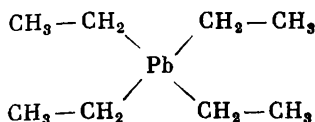
isooctane

The octane number of heptane is assumed to be zero, and that of isooctane, 100. If the octane number of a fuel is 80, this signifies that the fuel, when mixed with air (at the same compression ratio), knocks as a mixture consisting of 80% isooctane and 20% heptane.

The octane number of fuel is increased by raising its content of hydrocarbons with a branched chain of carbon atoms, and also by adding antiknocking agents, usually lead tetraethyl, a small amount of which considerably diminishes knocking.

* An increase in the compression ratio raises the power of an engine.

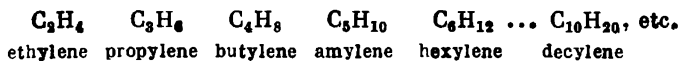
Tetraethyl lead is a heavy poisonous liquid whose molecules have the structure:



Tetraethyl lead belongs to organometallic compounds—substances in which the hydrocarbon radicals are directly bonded to an atom of a metal. These substances are finding greater and greater use.

51. Unsaturated Hydrocarbons

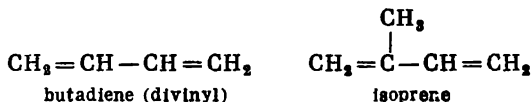
The simplest unsaturated hydrocarbon with a double bond—ethylene C_2H_4 ($\text{CH}_2=\text{CH}_2$), as indicated previously, is the parent of the homologous series of unsaturated **ethylene hydrocarbons***:



The composition of any hydrocarbon of this series is expressed by the general formula C_nH_{2n} (where n is the number of carbon atoms).

The composition of the members of the homologous series of unsaturated **acetylene hydrocarbons** (with a triple bond), whose parent is acetylene C_2H_2 ($\text{CH}\equiv\text{CH}$), is expressed by the general formula $\text{C}_n\text{H}_{2n-2}$.

The general formula $\text{C}_n\text{H}_{2n-4}$ also expresses the composition of hydrocarbons with two double bonds—**dienes**. Examples of those deserving special mention are **butadiene** (or **divinyl**) C_4H_6 and **isoprene** C_5H_8 :

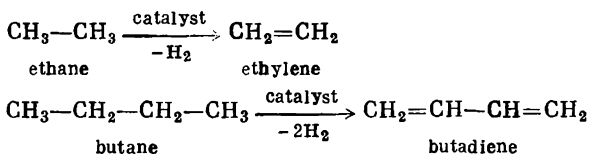


Hydrocarbons are known with a greater number of double bonds (**polyenes**) or triple ones (**polyynes**).

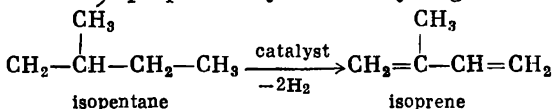
Unsaturated hydrocarbons can be prepared from saturated ones by the catalytic detachment of hydrogen (the reaction of **dehydrogenation**). For instance, ethylene is obtained from the ethane con-

* Previously, the ethylene hydrocarbons or alkenes were also called **olefins**, and hydrocarbons with two double bonds—**diethylenes** or **diolefins**. According to the IUPAC systematic nomenclature, hydrocarbons of the ethylene series are called **alkenes**, with two double bonds—**dienes**, while hydrocarbons of the acetylene series are called **alkynes**.

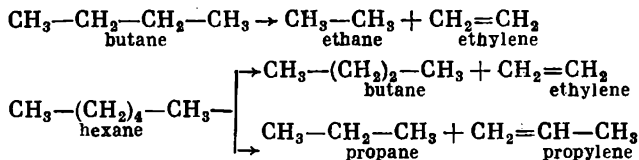
tained in casing head gas, and butadiene from butane:



Isoprene can be prepared by the dehydrogenation of isopentane:



The gaseous and liquid products of cracking of petroleum hydrocarbons are an important source for the production of ethylene and its homologues. **Cracking** is the name given to the process of cleaving hydrocarbons with long chains into molecules of a shorter length occurring in the presence of catalysts (**catalytic cracking**) or when saturated hydrocarbons are heated to 500-700 °C under pressure (**thermal cracking**). For example,

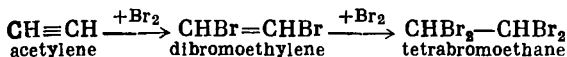
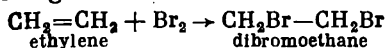


The cracking of petroleum products makes it possible to obtain mixtures of low-boiling hydrocarbons (for example, petrol) from hydrocarbons with a high boiling point. In cracking, unsaturated hydrocarbons are always obtained together with saturated ones. The unsaturated hydrocarbons formed in cracking, and also those produced by the dehydrogenation of saturated hydrocarbons contained in casing head gases, are finding greater and greater use in the industry of organic synthesis as a starting material for the production of plastics, chemical fibres, alcohols, rubber-like materials, detergents, solvents, and other valuable products.

The physical properties of the alkenes and alkynes vary in their homologous series with the same regularity as in the saturated hydrocarbons—the alkanes: the lower representatives are gases, next come liquids, and then substances with gradually growing melting and boiling points that are solids in ordinary conditions.

The unsaturated hydrocarbons sharply differ from their saturated counterparts in their chemical properties; they are exceedingly reactive and enter into a variety of combination reactions. Such reactions consist in the attachment of atoms or groups of atoms to the carbon atoms bonded by a double or triple bond. The multiple bonds break quite readily and transform into single ones.

For instance, ethylene and acetylene readily attach bromine, transforming into the relevant di- and tetrahalogen derivatives:



The reaction can be used for detecting unsaturated hydrocarbons—the reddish brown colour of bromine rapidly vanishes.

Another qualitative reaction showing the presence of multiple bonds is oxidation with potassium permanganate: unsaturated compounds are oxidized very readily with the breaking of their multiple bonds, and the purple colour of the KMnO_4 vanishes.

An important property of unsaturated hydrocarbons is the ability of their molecules to combine with one another or with molecules of other unsaturated hydrocarbons (a polymerization reaction, p. 170).

Ethylene C_2H_4 is a colourless gas with a weak pleasant odour, quite well soluble in water. Its boiling point is -103.8°C , and its freezing point is -169.5°C . It burns in air with a slightly glowing flame.

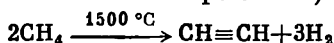
Ethylene is a very important starting material for the preparation of a number of synthetic products, especially of ethyl alcohol, ethylene oxide, ethylene glycol (antifreeze), polyethylene (p. 171), and others.

Acetylene C_2H_2 is a colourless gas with a characteristic weak odour. Its boiling and freezing points are -83.8°C and -80.8°C , respectively. Commercial acetylene produced from calcium carbide has an unpleasant odour due to the impurities in it. Acetylene burns in air with a greatly smoking flame, liberating a large amount of heat. This is why a mixture of acetylene and oxygen is widely used for the welding and cutting of metals (autogenous welding; the flame temperature reaches 3150°C). It is an explosion hazard; a mixture with air containing from 2.3 to 80.7% acetylene explodes from a spark. It dissolves with difficulty in water; under a small pressure (1.2 to 1.5 MPa) it dissolves quite well in acetone (up to 300 volumes) and is safe in this form.

The action of water on calcium carbide CaC_2 (see p. 107) is to date one of the widespread methods of producing acetylene:



A new modern method of producing acetylene is the pyrolysis (conversion at elevated temperatures) of hydrocarbons, chiefly methane:



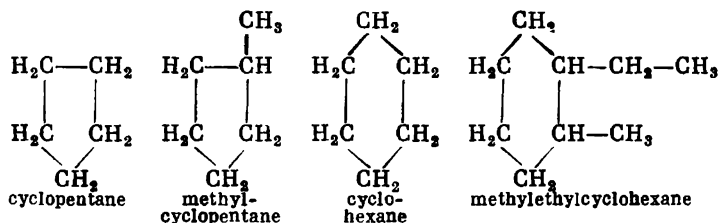
Acetylene, like ethylene, is a valuable chemical starting material. It is used to produce acetic aldehyde, ethyl alcohol, acetic acid, synthetic rubbers, plastics, and other products.

The investigations conducted by A. Favorsky (1860-1945) and his pupils in the field of unsaturated hydrocarbons, especially the alkynes, are of great significance. Favorsky discovered a great number of various regroupings of the molecules in chemical reactions and showed how to control these processes.

52. Saturated Cyclic Hydrocarbons (Cycloalkanes)

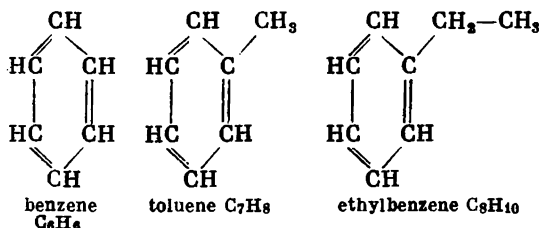
V. Markovnikov showed in the eighties of the 19th century that unlike American petroleum, the petroleum extracted in Baku contains mainly cyclic hydrocarbons having five or six carbon atoms in a ring. The carbon atoms in the molecules of these hydrocarbons are joined by single bonds as in the molecules of saturated hydrocarbons with an open chain—the alkanes or paraffins, which makes them similar in their properties to the latter. This is the reason why such cyclic hydrocarbons are now called cycloparaffins or, according to the IUPAC systematic nomenclature, **cycloalkanes**. They relate to the alicyclic compounds (p. 135).

Examples of cycloalkanes are:

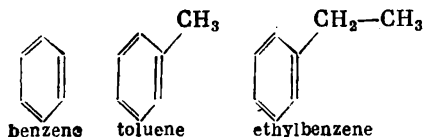


53. Aromatic Hydrocarbons

A very important group is formed by the cyclic hydrocarbons of the **aromatic series**; the simplest of them are benzene C_6H_6 and its homologues, for instance toluene (methylbenzene) $\text{C}_6\text{H}_5-\text{CH}_3$ and ethylbenzene $\text{C}_6\text{H}_5-\text{CH}_2\text{CH}_3$, whose composition corresponds to the general formula $\text{C}_n\text{H}_{2n-6}$, and whose structure is customarily expressed by the formulas

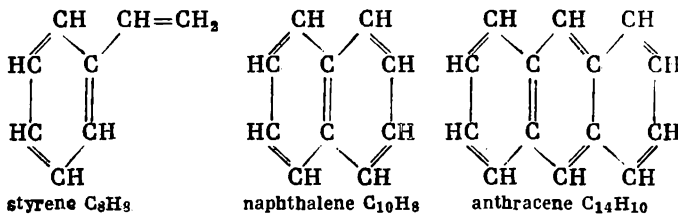


All these compounds contain a special cyclic grouping of six carbon atoms—the **benzene aromatic ring (nucleus)**. The structural formula of the benzene ring with three double and three single bonds alternating was proposed back in 1865 by the German chemist A. Kekule. To simplify its writing, the benzene ring is depicted by a hexagon in which the symbols C and H in the ring are omitted:



The monovalent benzene radical C_6H_5- , or , formed when a hydrogen atom is detached from any carbon atom of the benzene ring, is known as **phenyl**.

Aromatic hydrocarbons are known having multiple bonds in their side chains, for example **styrene**, and also **multinuclear** ones containing several benzene rings, for instance **naphthalene** and **anthracene**:



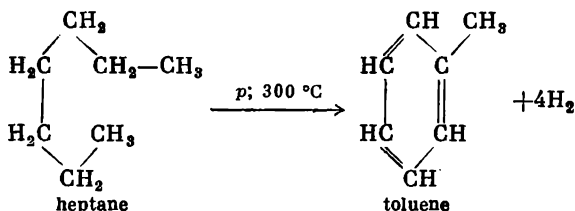
or in the simplified notation:



Aromatic hydrocarbons are contained in the coal tar produced in the coking of bituminous coal. Another important source for obtaining them is the petroleum of some deposits, for example of the Maikop one (USSR). To meet the enormous demand for aromatic hydrocarbons, they are also produced by the catalytic **aromatization** of the acyclic hydrocarbons of petroleum.

This problem was successfully solved by N. Zelinsky (see Vol. 1, p. 322) and his pupils B. Kazansky and A. Platé, who converted many saturated hydrocarbons into aromatic ones. For instance, heptane C_7H_{16} , when heated in the presence of a catalyst is converted into

toluene:

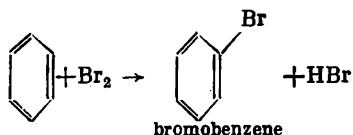


Aromatic hydrocarbons and their derivatives are widely used for the production of plastics, synthetic dyes, medicines and explosives, synthetic rubbers, and detergents.

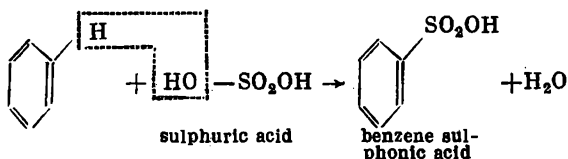
Benzene and all the compounds containing the benzene ring were called aromatic (at the beginning of the 19th century) because the first representatives of this series to be studied were fragrant substances or compounds separated from natural aromatic substances. At present, numerous compounds with no pleasant odour, but having a collection of chemical properties known as **aromatic properties**, are also included in this series.

Benzene is a colourless liquid with a characteristic odour. Its boiling and melting points are 80.1°C and 5.5°C , respectively. The aromatic properties of benzene determined by the features of its structure are expressed in the relative stability of the benzene ring notwithstanding the unsaturated composition of benzene. For example, unlike unsaturated compounds with alkene double bonds, benzene is stable to the action of oxidizing agents—like the saturated hydrocarbons, it does not decolourize a solution of potassium permanganate. Combination reactions are not characteristic of benzene. Conversely, benzene and the other aromatic compounds enter into reactions of replacement of hydrogen atoms in the benzene ring. The most important of these reactions are described below.

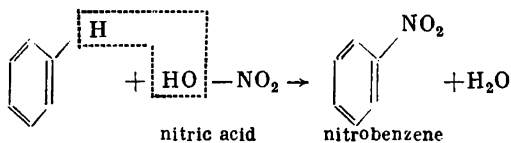
Halogenation Reaction. The action of bromine or chlorine (in the presence of catalysts) results in the formation of halogen derivatives:



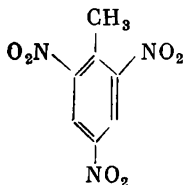
Sulphonation Reaction. The action of concentrated sulphuric acid (with heating) yields **sulphonic acids**:



Nitration Reaction. The action of concentrated nitric acid (in the presence of concentrated H_2SO_4) produces **nitrocompounds**:

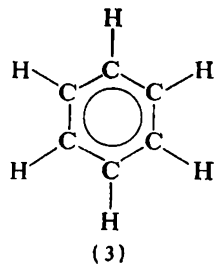
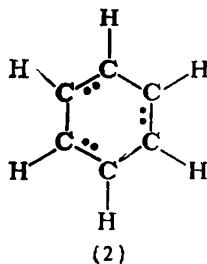
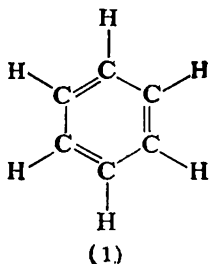


The nitration of toluene yields an explosive—**trinitrotoluene (trityl)**:



Many other aromatic **polynitrocompounds** (containing three and more nitro groups $-\text{NO}_2$) are also used as explosives. Nitrocompounds can be reduced to amines (Sec. 61).

It follows from the above that formula (1) of benzene (see below) in the form of a ring with alternating double and single bonds (Kekulé's formula) does not accurately express the nature of the bonds between the carbon atoms in the benzene ring. According to this formula, benzene must have three localized pi bonds, i.e. three pairs of pi electrons each of which is fixed in place between two carbon atoms. If these pi electrons are designated by dots, the structure of benzene can be represented by formula (2):



Experiments show, however, that the benzene ring does not have the usual double bonds alternating with single ones, and that all the bonds between the carbon atoms in benzene are equivalent. The length of each of them (0.140 nm) is intermediate between the length of a single C—C bond (0.154 nm) and that of the alkene double bond C=C (0.134 nm) in other (non-aromatic) organic compounds.

Each of the carbon atoms in the benzene ring is in the state of sp^2 hybridization and uses three valence electrons to form sigma bonds

with the two adjacent carbon atoms and with one hydrogen atom. All six carbon atoms and all the sigma bonds C—C and C—H are in one plane (Fig. 27). The cloud of the fourth valence electron of each of the carbon atoms (i.e. the cloud of the p electron not participating in hybridization) has the shape of a dumbbell and is oriented at right angles to the benzene ring plane. Each of such p electron clouds overlaps above and under the plane of the ring with the p electron clouds of the two adjacent carbon atoms. This is shown in Fig. 28a and, in projection, in Fig. 28b. The density of the pi electron clouds in benzene is distributed uniformly between all the C—C bonds. In other words, the six pi electrons are shared by all the carbon atoms of the ring and form a single annular cloud (an **aromatic electron sextet**). This is how the equivalence (levelling out) of the aromatic bonds giving rise to the characteristic (aromatic) properties of the benzene ring is explained. The uniform distribution of the

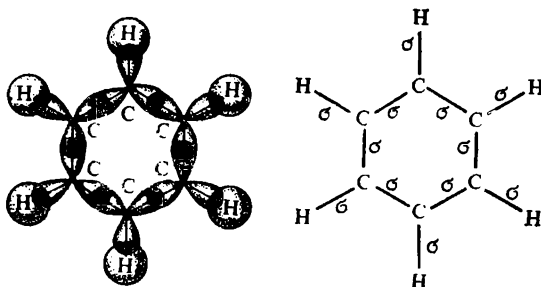


Fig. 27. Formation of sigma bonds in a benzene molecule

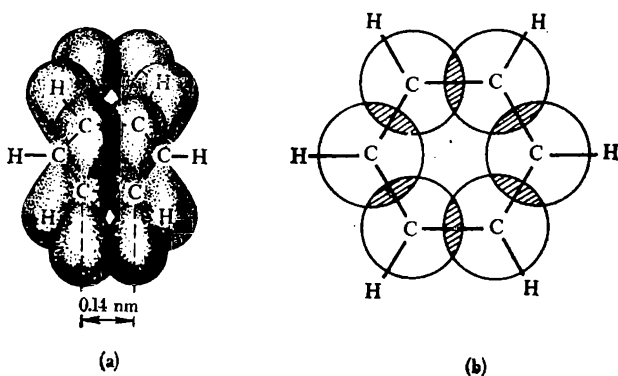


Fig. 28. Overlapping of pi-electron clouds in a benzene molecule

cloud of pi electrons and the levelling out of the bonds in benzene are sometimes depicted by formula (3) (see above).

Accordingly, instead of the generally adopted symbol of the benzene ring in the form of a hexagon with alternating double and single bonds corresponding to Kekule's formula (1a), benzene is depicted by a hexagon with a circle inside (3a):

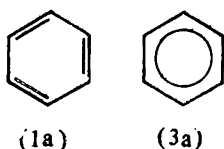
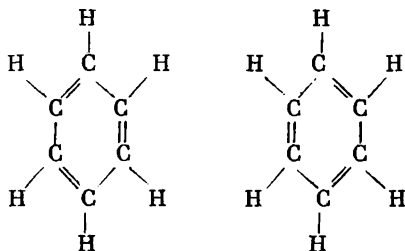


Figure 29 shows a segment model of a benzene molecule.

From the viewpoint of the method of superposition of valence (electron dot) formulas, the structure of the benzene molecule represented by formula (3) should be considered as an intermediate one between the two possible structures of benzene expressed by the Kekule formulas:



Since in the benzene molecule three electron pairs are shared by all six carbon atoms of the benzene ring, the bonds they form are six-centered ones (see Vol. 1, Sec. 44).

54. Halogen Derivatives of Hydrocarbons

Halogen derivatives are compounds that can be considered as the products of replacement of one or more hydrogen atoms in a hydrocarbon molecule by

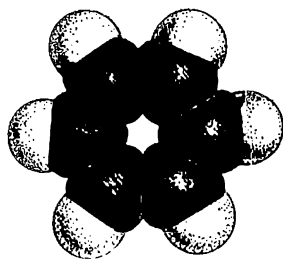


Fig. 29. Segment model of a benzene molecule

halogen atoms. Examples of this class of compounds are given below.

Methylene dichloride (dichloromethane) CH_2Cl_2 is a liquid boiling at 40.1°C . It is used as a solvent.

Chloroform (trichloromethane) CHCl_3 is a liquid boiling at 61.2°C . It is used for narcosis in surgical operations and as a solvent.

Carbon tetrachloride (tetrachloromethane) CCl_4 is a heavy non-combustible liquid boiling at 76.8°C . It is used as a solvent in extracting fats and oils from plants, for removing grease spots from clothes, and in fire extinguishers.

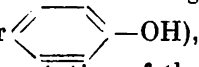
Diffuorodichloromethane (Freon-12) CF_2Cl_2 is a liquid boiling at 29.8°C . It is not poisonous and does not react at room temperature with metals. When it evaporates, it absorbs a large amount of heat. It is used (like other Freons—polyfluorochlorohydrocarbons) in refrigerating installations, and also as a solvent for the formation of aerosols.

Vinyl chloride $\text{CH}_2=\text{CH}-\text{Cl}$ is a derivative of ethylene. It is a colourless gas. It is produced by attaching hydrogen chloride to acetylene. It is readily polymerized and is used for the production of polyvinyl chloride (p. 172).

Tetrafluoroethylene $\text{CF}_2=\text{CF}_2$ is a colourless gas. It is produced by the pyrolysis of Freon-22 (CHF_2Cl) and is used in the production of fluoroplastics (p. 172).

Some halogen derivatives of hydrocarbons are included in the composition of poisonous chemicals—chemical means for combatting harmful insects (**insecticides**) and fungi infecting plants (**fungicides**).

55. Alcohols and Phenols

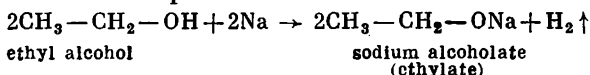
Alcohols are derivatives of saturated or unsaturated hydrocarbons in whose molecules one or several hydrogen atoms are replaced by hydroxyl groups*. For instance, methyl alcohol (methanol) CH_3-OH is a hydroxyl derivative of methane CH_4 , ethyl alcohol (ethanol) $\text{CH}_3-\text{CH}_2-\text{OH}$ is a derivative of ethane CH_3-CH_3 . Derivatives of aromatic hydrocarbons with the group OH in the benzene ring are called **phenols**. For instance, **phenol** $\text{C}_6\text{H}_5-\text{OH}$ (or  $-\text{OH}$), a derivative of benzene C_6H_6 , is the simplest representative of the class of phenols.

Like water molecules (see Vol. 1, Sec. 70), the molecules of the lower alcohols are joined to one another by hydrogen bonds. Hence,

* The alcohols also include the derivatives of cycloalkanes (for example, cyclohexanol $\text{C}_6\text{H}_{11}\text{OH}$ —a derivative of cyclohexane C_6H_{12}), and the derivatives of aromatic hydrocarbons containing the OH group in a side chain instead of in the benzene ring (for example, the aromatic benzyl alcohol $\text{C}_6\text{H}_5-\text{CH}_2-\text{OH}$ is a derivative of toluene $\text{C}_6\text{H}_5-\text{CH}_3$).

they are associated liquids and have higher boiling points than the hydrocarbons whose derivatives they are, and than other organic substances having the same composition and molecular mass, but not containing hydroxyl groups. Phenols in ordinary conditions, as a rule, are crystals.

A common property of alcohols and phenols is the mobility of the hydroxyl group hydrogen. For instance, when an alcohol is reacted with an alkali metal, this hydrogen is replaced by the metal, and solid compounds are produced called **alcoholates** that are soluble in alcohol. An example is:

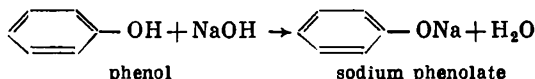


Formally, such a reaction reminds one of the formation of salts from acids, but alcoholates are similar to salts of very weak acids and are completely hydrolyzed by water to form an alcohol and an alkali again:



This is the reason why no alcoholates are formed when alcohols react with aqueous solutions of alkalis.

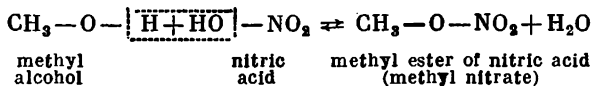
In phenols, the mobility of the hydroxyl group hydrogen is higher under the influence of the aromatic benzene ring. They form metal derivatives—**phenolates**—not only when reacted with alkali metals, but also, unlike alcohols, when reacted with alkalis:



Phenolates, unlike alcoholates, are not decomposed by water, but in aqueous solutions they too, like salts of weak acids and strong bases, are partly hydrolyzed, and their solutions have an alkaline reaction. A phenol is displaced from a phenolate even by carbonic acid.

Alcohols are essentially not electrolytes. The dissociation constant of ethyl alcohol is close to 10^{-18} , whereas the dissociation constant of water is close to 10^{-16} , i.e. ethyl alcohol is a weaker acid than water. The dissociation constant of phenol is somewhat higher (1.3×10^{-10}).

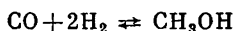
Alcohols and phenols react with acids to form esters, for example:



Of special interest are the esters of alcohols and phenols with organic acids (see Sec. 59).

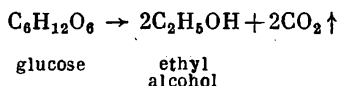
Alcohols are oxidized considerably more easily than the relevant hydrocarbons. Here aldehydes or ketones are formed (p. 155).

Methyl alcohol or **methanol** CH_3OH is a colourless liquid boiling at 64.5°C . *It is very poisonous*: small oral doses of it cause blindness, and large ones—death. Methyl alcohol is synthesized in large quantities from carbon dioxide and hydrogen at a high pressure (20–30 MPa) and temperature (400°C) in the presence of a catalyst (about 90% ZnO and 10% Cr_2O_3):



Methyl alcohol is also formed in the dry distillation of wood; this is why it is also known as **wood alcohol**. It is used as a solvent, and for producing other organic substances.

Ethyl alcohol or **ethanol** $\text{CH}_3\text{CH}_2\text{OH}$ (boiling point 78.4°C) is one of the most important starting substances in the modern industry of organic synthesis. It has been prepared from time immemorial using various sugar-containing substances such as grape sugar or glucose that transforms into ethyl alcohol by “fermentation” caused by ferments (enzymes) produced by yeast fungi. The reaction follows the formula

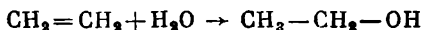


Glucose is contained, for example, in the free state in grape juice, upon whose fermentation grape wine containing from 8 to 16% alcohol is obtained.

The starting material for the production of alcohol may be the polysaccharide starch (p. 164) contained, for instance, in the tubers of potatoes, and in the grain of rye, wheat, and corn. To convert the starch into saccharide substances (glucose), it is first hydrolyzed. For this purpose, flour or crushed potatoes are scalded with hot water and cooled. After this, **malt**—germinated barley grains that are dried and then ground with water—is added. The malt contains **diastase** (a complex mixture of enzymes) that catalyzes the saccharization of the starch. Upon completion of the saccharization, yeast is added to the liquid obtained, and its enzyme (**zimase**) causes alcohol to be formed. It is distilled off and then purified by redistillation.

At present, another polysaccharide—cellulose, which forms the main part of wood, is also saccharized. To do this, cellulose is hydrolyzed in the presence of acids (for example, sawdust is treated at $150\text{--}170^\circ\text{C}$ with 0.1–5% sulphuric acid under a pressure of 0.7–1.5 MPa). The product also contains glucose and is fermented into alcohol with the aid of yeast (**hydrolysis alcohol**).

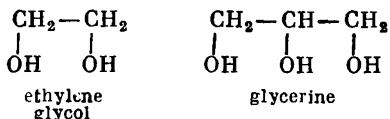
Finally, ethyl alcohol can be prepared synthetically from ethylene. The net reaction consists in the addition of water to ethylene (in the presence of catalysts):



Recent years have seen the construction of plants synthesizing ethyl alcohol from ethylene and an increase in the production of alcohol from wood in the USSR. This made it possible to save a large amount of food products*.

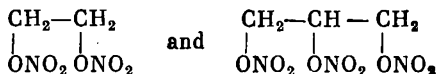
In addition to alcohols with one hydroxyl group in a molecule (monatomic alcohols), alcohols are known whose molecules contain several hydroxyl groups (polyatomic alcohols).

Examples are the diatomic alcohol **ethylene glycol** and the triatomic alcohol **glycerine (glycerol)**:



Ethylene glycol and glycerine are high-boiling liquids with a sweet taste mixing with water in any proportions. Ethylene glycol is used as a component of **antifreezes**, i.e. substances having a low freezing point and replacing water in the radiators of motor vehicles and aircraft in cold weather. An aqueous solution of ethylene glycol (58%) freezes only at -50°C . Ethylene glycol is also employed for the preparation of the synthetic fibre Lavan (Dacron or Terylene, p. 176). *It is very poisonous when taken orally.*

The nitric ethers of ethylene glycol and glycerine



whose trivial names are nitroethylene glycol and nitroglycerine, are strong explosives and are used in the manufacture of dynamites.

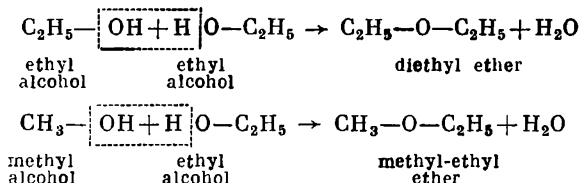
Phenol $\text{C}_6\text{H}_5\text{OH}$ forms colourless crystals melting at 41°C . It has a characteristic odour and antiseptic (disinfecting—suppressing the development of harmful microorganisms) properties. We have already indicated that the acid properties of hydroxyl hydrogen are displayed much more strongly in phenol than in alcohols; this hydrogen can be replaced with a metal not only in reactions with alkali metals, but also with alkalies. For this reason, phenol is also known as **carbolic acid**.

Phenol is contained in coal tar, and is also prepared synthetically from benzene. It is used in large amounts for the synthesis of drugs, dyes, plastics (phenolic plastics, p. 175), and for purifying petroleum lubricating oils.

* From 5500 tonnes of dry sawdust (the residues of a medium capacity sawmill during a year), it is possible to produce 790 tonnes of alcohol (reduced to the 100% product). This allows about 3000 tonnes of grain or 10 000 tonnes of potatoes to be saved.

56. Ethers

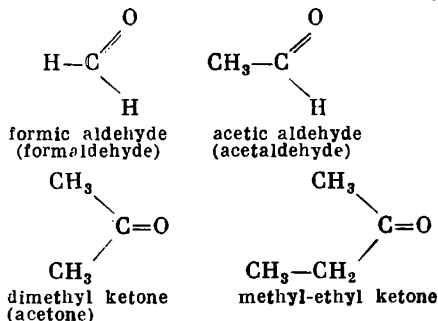
Ethers are defined as organic compounds whose molecules consist of two hydrocarbon radicals joined by an oxygen atom. They are usually prepared catalytically by detaching a molecule of water from two molecules of the same or different alcohols. For example:



Most ethers are liquids almost insoluble in water. They are quite inert in a chemical respect: unlike alcohols, they have no mobile hydrogen, therefore they do not react with metallic sodium; unlike esters (see Sec. 59), they do not become hydrolyzed. The most important of the ethers is **diethyl ether** $(\text{C}_2\text{H}_5)_2\text{O}$ —a mobile liquid with a characteristic odour boiling at 35.6°C . It is widely used as a solvent, and in medicine for narcosis and as a constituent of certain drugs.

57. Aldehydes and Ketones

Molecules of these compounds contain the divalent carbonyl group >C=O . In aldehydes, it is joined to one H atom and to a hydrocarbon radical*, and in ketones to two hydrocarbon radicals:

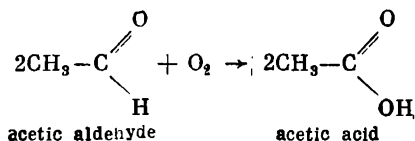


The presence of the carbonyl group in both aldehydes and ketones underlies the definite similarity of their properties. There are also differences, however, associated with the fact that one of the bonds of the carbonyl group in aldehyde molecules is used for joining hydrogen. Therefore, they contain a special **aldehyde functional**

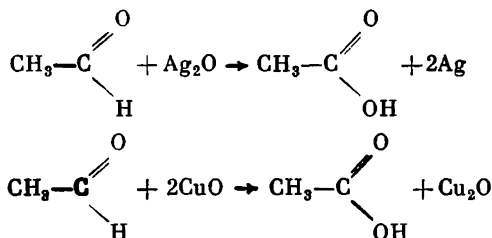
* In formic aldehyde, the carbonyl group is joined to two hydrogen atoms

group $\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—} \\ | \\ \text{H} \end{array}$ (or —CH=O). Aldehydes are very readily oxidized

at the expense of the hydrogen of this group and transform into carboxylic acids (see the following section). For instance, when acetic aldehyde is oxidized, acetic acid is formed, which is widely used in industry and domestically:

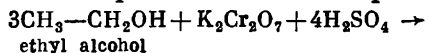


Owing to their property of being readily oxidized, aldehydes are vigorous reducing agents; in this they appreciably differ from ketones, which are oxidized much more difficultly. For example, aldehydes reduce silver(I) oxide to metallic silver (the “silver mirror” reaction—the silver is deposited on the walls of the vessel forming a mirror coating) and copper(II) oxide to copper(I) oxide*:

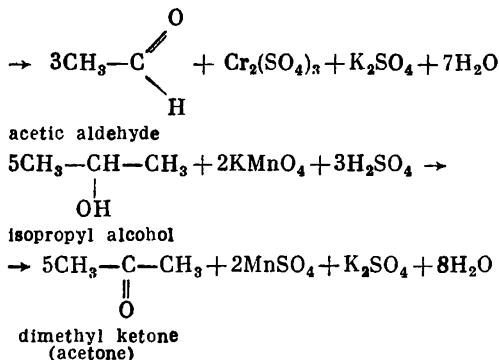


Ketones are not oxidized in these conditions, therefore the two reactions are used as qualitative ones allowing aldehydes to be distinguished from ketones.

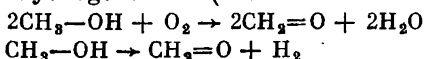
Aldehydes and ketones can be prepared by oxidizing the relevant alcohols, i.e. those having the same carbon skeleton and the hydroxyl group at the carbon atom that forms the carbonyl group in the aldehyde or ketone produced. For example:



* Silver(I) oxide is generally used for these reactions in the form of its colourless solution in aqueous ammonia. Such a solution contains the complex compound $[\text{Ag}(\text{NH}_3)_2]\text{OH}$. The copper(II) oxide is taken in the form of an alkaline solution of its complex compound with tartaric acid (Fehling's solution—a blue solution); the copper(I) oxide precipitates as a red sediment; the blue colour of the reagent vanishes.

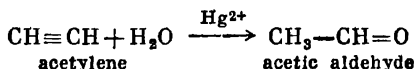


Formic aldehyde, or **formaldehyde** $\text{CH}_2=\text{O}$ is a gas with a sharp unpleasant odour that is well soluble in water. It has antiseptic and also tanning properties. An aqueous solution of formaldehyde (usually 40%) is called **formalin**. It is widely used for disinfection, preserving anatomical preparations, for treating seeds before sowing, etc. Considerable amounts of formaldehyde are used to prepare phenol-formaldehyde resins (p. 175). Formaldehyde is produced from methyl alcohol by catalytically oxidizing it with the oxygen of the air or by dehydrogenation (the detachment of hydrogen):



These reactions proceed when methyl alcohol vapour (in the first case mixed with air) is passed over heated catalysts.

Acetic aldehyde, or **acetaldehyde**, $\text{CH}_3-\text{CH}=\text{O}$, is a low-boiling colourless liquid (boiling point 21°C) with a characteristic odour of rotten apples, well soluble in water. In industry, it is prepared by adding water to acetylene in the presence of mercury(II) salts as a catalyst:



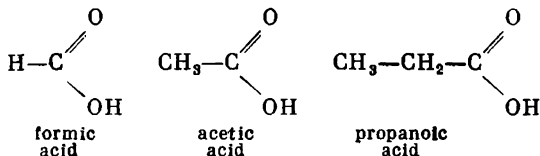
This reaction, which is of great practical significance, was discovered by M. Kucherov (1850-1911). Acetic aldehyde can then be oxidized to acetic acid; it is also used for many other syntheses.

Acetone, or **dimethylketone**, $\text{CH}_3-\text{CO}-\text{CH}_3$, is a colourless liquid with a characteristic odour boiling at 56.2°C . It mixes with water in any proportions. It is a very good solvent for many organic substances. It is widely used in the paint, lacquer, and varnish industry, in the production of some kinds of artificial fibre, shatter-proof organic glass, motion picture films, smokeless powder, and for dissolving acetylene (in cylinders).

Acetone is also used as the starting substance for the synthesis of a number of organic compounds.

58. Carboxylic Acids

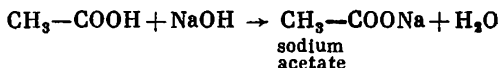
These compounds are characterized by the presence in the relevant molecules of the **carboxyl group (carboxyl)** $\text{—C}\begin{smallmatrix} \text{O} \\ \text{OH} \end{smallmatrix}$, or simpler —COOH , which is the functional group of this class of compounds. Examples of these acids are:



Inspection of the above formulas shows that the complex carboxyl group is a combination of the carbonyl $\text{—C}\begin{smallmatrix} \text{O} \\ \text{OH} \end{smallmatrix}$ and hydroxyl —OH groups. The latter under the influence of the carbonyl group differs appreciably from the hydroxyl group of alcohols, and the hydrogen in it detaches in the form of a cation in aqueous solutions. Carboxylic acids undergo electrolytic dissociation, for example:



These acids form salts with bases:



Carboxylic acids are weak acids, consequently their salts undergo reversible hydrolysis. Depending on the number of carboxyl groups in a molecule, carboxylic acids are divided into monobasic, dibasic, etc. acids.

Carboxylic acids, like inorganic acids, produce esters with alcohols (see the following section), and they are often encountered in this form in natural products.

Acetic acid $\text{CH}_3\text{—COOH}$ (anhydrous) is a liquid with a pungent irritating odour boiling at 118.1°C . At $+16.7^\circ\text{C}$, it freezes into a crystalline mass resembling ice (100%, or “glacial” acetic acid). It mixes with water in any proportions. It is widely used as a condiment and a preservative. It is sold for domestic use in the form of an 80% (vinegar essence) and 9% (vinegar) aqueous solution. The long known **natural or wine vinegar** is a product containing acetic acid and obtained in the souring of grape vine (as a result of the

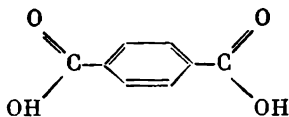
microbiological oxidation of the ethyl alcohol contained in the wine). Acetic acid is also used in many syntheses and as a solvent. At present, both domestic and technical acetic acid is chiefly synthesized from acetylene—by adding water to it according to the Kucherov reaction (see above) and oxidizing the acetaldehyde formed.

Higher Fatty Acids. These acids include saturated and unsaturated carboxylic acids with a straight carbon atom chain containing 16, 18, and more carbon atoms; natural fats contain acids of this kind (see the following section). The most important of them are the following saturated acids: **palmitic acid** $C_{15}H_{31}COOH$, or $CH_3(CH_2)_{14}COOH$, and **stearic acid** $C_{17}H_{35}COOH$, or $CH_3(CH_2)_{16}COOH$, and also the unsaturated **oleic acid** $C_{17}H_{33}COOH$, or $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$. The higher saturated acids are wax-like substances, and the unsaturated ones are liquids (resembling vegetable oil). The sodium and potassium salts of the higher fatty acids are called **soaps** (for instance, $C_{17}H_{35}COONa$ —sodium stearate, $C_{15}H_{31}COOK$ —potassium palmitate, etc.). Sodium soaps are solid, and potassium ones, liquid.

Benzoic acid C_6H_5-COOH , or  $-COOH$, is the simplest monobasic acid of the aromatic series. It forms colourless crystals (plates) melting at $121.5^\circ C$. It is an antiseptic. It is used for preserving food products, and also in many organic syntheses.

Oxalic (ethanedioic) acid $HOOC-COOH$ is the simplest dibasic carboxylic acid. It is a crystalline substance (the anhydrous acid melts at $189^\circ C$, and the dihydrate $C_2H_2O_4 \cdot 2H_2O$ at $101.5^\circ C$). It dissolves in water, and is poisonous. It is contained in many plants in the form of the potassium hydrogen salt. It is used in dyeing fabrics.

Terephthalic acid $HOOC-C_6H_4-COOH$ is a dibasic carboxylic acid of the aromatic series. Its structural formula is:



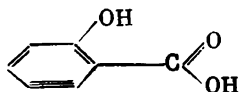
The synthetic fibre Laysan (Terylene, Dacran) (see Sec. 63) is produced from terephthalic acid and ethylene glycol (see Sec. 55).

Lactic acid $CH_3-CH-COOH$ is an example of compounds with



mixed functional groups—it exhibits the properties of an acid and an alcohol (an alcohol-acid). It is formed in the lactic fermentation of sugar-containing substances caused by special bacteria. It is contained in sour milk, the brine of sauerkraut, and siloed fodder.

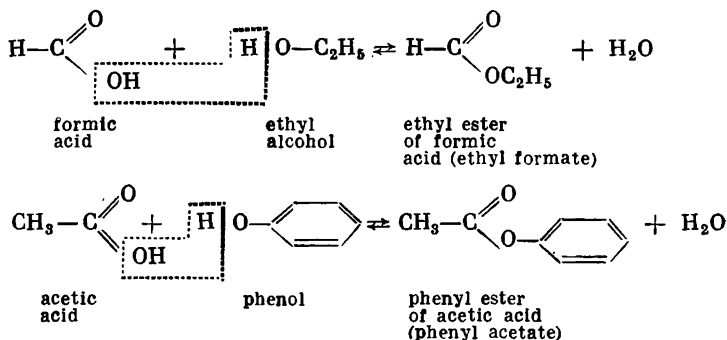
Salicylic acid $\text{HO}-\text{C}_6\text{H}_4-\text{COOH}$ is the analogue of lactic acid in the aromatic series. It has the structure



It belongs to compounds with mixed functional groups—it exhibits the properties of an acid and a phenol (a phenol-acid). It is an antiseptic. It is used (especially its salts and esters) as a drug, and also in many syntheses.

59. Carboxylic Acid Esters. Fats

The products of the reaction of carboxylic acids with alcohols or phenols are esters. For instance:



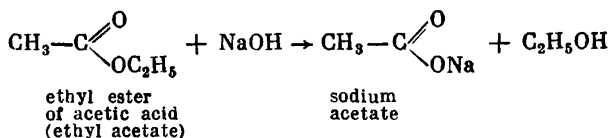
The reaction of formation of an ester from an acid and an alcohol (or phenol) is called an **esterification** reaction. It is catalyzed by hydrogen ions and is therefore accelerated in the presence of mineral acids.

Esters are insoluble (or almost insoluble) in water, but dissolve in organic solvents. Their solutions do not conduct an electric current.

Esters, unlike ethers, are decomposed by water at a certain rate—they are **hydrolyzed** with the formation of an acid and an alcohol (or phenol) again. Consequently, as shown in the equations of the above reactions, esterification is reversible and reaches a state of dynamic equilibrium. Hydrogen ions, like any catalyst (see Vol. 1, Sec. 60), accelerate not only the esterification reaction, but also the reverse reaction of hydrolysis. Hence, equilibrium in esterification is reached more rapidly in the presence of a mineral acid.

The hydrolysis of esters is increased by hydroxide ions. When heated with alkalis, esters decompose to form an alcohol (or phenol)

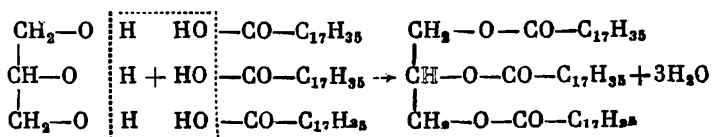
and a salt of the acid:



The reaction of the alkaline hydrolysis of esters is known as a **saponification** reaction.

Many esters of carboxylic acids and saturated alcohols have a pleasant odour and are often encountered in plants, imparting a fragrance to flowers, and an aroma to fruit and berries. Some of the esters are produced artificially and under the name of "fruit essences" are widely used in confectionery, in the manufacture of soft beverages, and in the perfume industry. Isoamyl acetate $\text{CH}_3\text{COOC}_5\text{H}_{11}$ (oil of pears) is used as a solvent of celluloid and other plastics.

Fats. Natural animal and vegetable fats (the latter are customarily called oils) are mixtures of esters formed by the higher fatty acids (see the preceding section) and the triatomic alcohol glycerine. Below is shown the formation of the ester of glycerine and stearic acid:



The composition of solid fats mainly includes esters of the saturated (palmitic and stearic) acids and that of liquid vegetable oils, esters of an unsaturated (oleic) acid. Hydrogen (in the presence of nickel as a catalyst) causes liquid fats to transform into solid ones owing to the attachment of hydrogen at the place of the double bond between the carbon atoms in the esterified molecules of the unsaturated acid. This process is known as the **hydrogenation** or **solidification** of fats and is used, for instance, to produce **margarine**, employed as a substitute of butter, from vegetable oils.

Like all esters, fats are liable to hydrolysis (saponification). The hydrolysis of fats, which proceeds slowly by itself, is catalyzed by strong acids and enzymes formed in living organisms. Alkalies also facilitate the hydrolysis of fats.

When a fat is hydrolyzed in a neutral or acid medium, the products are glycerine and the acids indicated above, while when it is hydrolyzed in an alkaline medium, the products include the salts of the free acids—soaps (see the preceding section) instead of the free acids themselves.

Some oils, for example **linseed oil**, consist of esters of glycerine and unsaturated higher acids whose molecules contain two or three double bonds each ("highly saturated" or "polysaturated" fatty acids). Such oils are oxidized in air and when applied to a surface form solid and strong films. They are called **drying oils**. To speed up the drying process, the oils are preliminarily boiled with an addition of **siccatives**—oxides of metals (cobalt, manganese, or lead) that are catalysts in the process of film formation. This is how the drying oil used in the manufacture of oil paints is obtained.

Fats are used for many technical purposes. But of especially great significance is their use as an important constituent part of the food ration of man and animals in addition to carbohydrates (see the following section) and proteins (see Sec. 62). The discontinuation of the use of food fats in engineering and their replacement with non-edible substances is one of the very important problems of the national economy.

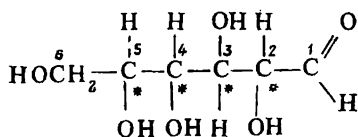
60. Carbohydrates

Carbohydrates include sugars and substances converted into them in hydrolysis. Carbohydrates are products of a vegetable and animal origin. In addition to proteins and fats, they are a very important constituent part of the food of man and animals; many of them are used as a technical raw material. Carbohydrates are classified into monosaccharides, disaccharides, and polysaccharides.

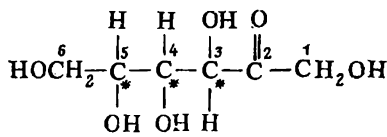
Monosaccharides are the simplest carbohydrates. They do not lend themselves to hydrolysis—they are not decomposed by water into simpler carbohydrates.

Glucose, or **grape sugar**, $C_6H_{12}O_6$, is the most important of the monosaccharides. It forms white crystals with a sweet taste that readily dissolve in water. It is contained in grape juice, in many kinds of fruit, and also in the blood of man and animals. Muscular work is done chiefly at the expense of the energy evolved when glucose is oxidized.

Glucose is a hexatomic aldehyde-alcohol; its structure can be represented by formula (a):



glucose
(a)



fructose
(b)

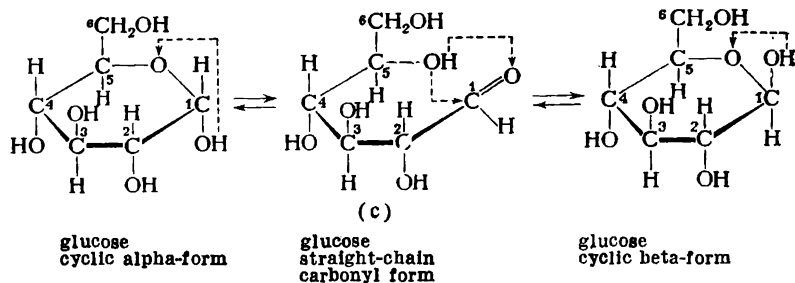
Glucose is obtained in the hydrolysis of the polysaccharides starch and cellulose (under the action of enzymes or mineral acids).

It is used to provide a high-caloric diet or as a medicine, in the finishing of fabrics, and as a reducing agent in the manufacture of mirrors.

Fructose, or fruit sugar, $C_6H_{12}O_6$, is a monosaccharide that accompanies glucose in many fruit and berry juices. It is much sweeter than glucose. Honey contains a mixture of these two monosaccharides. It is a hexatomic ketone-alcohol; its structure is expressed by formula (b) given above.

The formulas of glucose (a) and fructose (b) show the relative spatial arrangement of the H atoms and OH groups at the asymmetrical (p. 131) carbon atoms (marked with an asterisk) in the carbon chain characteristic of these monosaccharides.

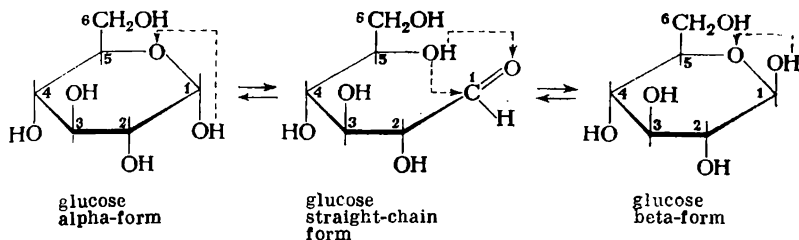
Monosaccharides, being aldehyde- or ketone-alcohols, are compounds with mixed functional groups. Their nature is made more complicated by the possibility of intramolecular reactions between the alcohol hydroxyl groups and the aldehyde or ketone carbonyl group. As a result, monosaccharides exist and enter into a reaction not only in the straight-chain form, but also in cyclic forms. The carbon chain of a monosaccharide, for instance glucose (a), can take on the conformation (p. 126) of a "claw" (see formula c below); the first carbon atom carrying the carbonyl group approaches the alcohol group at the fifth carbon atom; the hydrogen atom from the OH group moves (as shown by the dotted arrow) to the carbonyl oxygen, while the oxygen at the fifth carbon atom combines with the first (carbonyl) carbon atom (this is also shown by a dotted arrow). As a result, the six-membered ring containing an oxygen atom closes. In this way, two cyclic **alpha**- and **beta**-forms of glucose are produced that differ in the spatial arrangement of the H atom and the OH group at the first carbon atom (which becomes asymmetrical in the ring). This can be depicted by the perspective formulas*:



Perspective formulas are more often written in a simplified way, without the symbols of the C's forming the ring and the H's bonded

* In perspective formulas, the atoms forming a ring are arranged, as it were, in a horizontal plane perpendicular to the plane of the drawing; the thick lines designate the bonds between the atoms of the ring extending forward towards the observer.

to them:



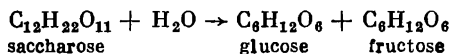
The formulas of the cyclic forms show (the dotted arrow) that the reverse transition of the H atom from the OH group at the first carbon atom to the oxygen of the ring is possible. The ring opens, and the straight-chain form is produced.

Natural crystalline glucose (grape sugar) is the cyclic α -form (the melting point of the monohydrate is 83°C , and of the anhydrous form is 146°C). When dissolved in water, it transforms into the straight-chain form, as shown above in the formula, and through it to the β -form; dynamic equilibrium sets in between all the forms*. The β -form can also be separated in the crystalline state (its melting point is $148\text{--}150^\circ\text{C}$). In an aqueous solution, it also produces an equilibrium system containing all the forms. The straight-chain form exists only in solutions, in very small amounts (fractions of a per cent), and has not been separated in the free state.

Isomeric forms of compounds capable of transforming into one another are called **tautomeric forms**, or **tautomers**, and their very existence is known as the phenomenon of **tautomerism**; it is quite widespread among organic compounds.

Disaccharides are carbohydrates that when heated with water in the presence of mineral acids or under the influence of enzymes become hydrolyzed and decompose into two monosaccharide molecules.

Beet, or cane sugar (saccharose), $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, is the most important of the disaccharides. It is produced from sugar beets (containing up to 28% saccharose of the dry matter) or from sugar cane (whence the names occur). It is also contained in the sap of birch and maple trees and in some kinds of fruit. Saccharose is a very valuable food product. It hydrolyzes into a molecule of glucose and one of fructose (the mixture of these monosaccharides formed is called **inverted sugar**):



* In an equilibrium system of monosaccharides, their cyclic forms with a five-membered oxygen-containing ring are also produced. They are unstable and have not been recovered in the free crystalline state. But many natural and synthetic compounds that are derivatives of five-membered cyclic forms of the monosaccharides are known (see textbooks on organic chemistry).

Polysaccharides. These carbohydrates differ in many respects from mono- and disaccharides—they have no sweet taste, and most of them are insoluble in water. They are complex high-molecular compounds that hydrolyze under the catalytic influence of acids or enzymes with the formation of simpler polysaccharides, then disaccharides, and, in the long run, a multitude (hundreds and thousands) of molecules of monosaccharides. The most important representatives of the polysaccharides are starch and cellulose. Their molecules are built up of the units $\text{—C}_6\text{H}_{10}\text{O}_5\text{—}$. These are residues of six-membered cyclic forms of glucose molecules that have lost a water molecule. Hence, the composition of both starch and cellulose is expressed by the general formula $(\text{C}_6\text{H}_{10}\text{O}_5)_x$. The difference between the properties of these polysaccharides is due to the spatial isomerism of the monosaccharide molecules forming them: starch is built up of units of the alpha-form, and cellulose of units of the beta-form of glucose (see textbooks on organic chemistry).

Starch $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ is a white (granulated in a microscope) powder insoluble in cold water; in hot water it swells and forms a colloidal solution (starch paste); when treated with an iodine solution, it becomes blue (a characteristic reaction). Starch molecules are not uniform in size—the value of x in them fluctuates from hundreds to 1000-5000 and more.

Starch is formed as a result of photosynthesis in the leaves of plants; it is also deposited “as a reserve” in tubers, roots, and grains. In the digestive tract of man and animals, starch is hydrolyzed and transforms into glucose, which is assimilated by the organism.

In industry, starch is converted into glucose (the **saccharification** process) by boiling it for several hours with dilute sulphuric acid (the catalytic influence of sulphuric acid on the saccharification of starch was discovered in 1811 by the Russian scientist K. Kirchhoff). The acid is removed from the solution by adding chalk to it, which forms insoluble calcium sulphate with the acid. The sulphate is filtered off, and the solution is evaporated. The thick sweet mass obtained, known as **starch molasses**, contains a considerable amount of the products of starch hydrolysis in addition to glucose. Molasses is used to prepare confectionary products and for a variety of technical purposes.

When pure glucose is needed, the starch is boiled longer, which converts it more completely into glucose. The solution obtained after neutralization and filtration is condensed until glucose crystals begin to precipitate from it.

If dry starch is heated to 200-250 °C, it partly decomposes, and the result is a mixture of less complex polysaccharides than starch called **dextrin**. The latter is used for finishing fabrics and for producing glue. The transformation of starch into dextrin explains the

formation of the shiny crust on baked bread, and also the lustre of starched linen.

Cellulose ($C_6H_{10}O_5$)_x is a fibrous substance, the main constituent of the shells of plant cells. The value of *x* in cellulose molecules is usually about 3000, but it may reach 6000 to 12 000. The purest natural cellulose—cotton fibre—contains from 85 to 90% cellulose. The wood of softwood species contains about 50% of cellulose (wood, in addition to cellulose, contains its companions, the most important of which are **lignin**—a natural polymer built up of several aromatic oxygen-containing compounds of the benzene series, and **hemicelluloses**—other polysaccharides that are relatives of cellulose).

Cellulose is very important. It is sufficient to mention that an enormous amount of cotton fibre is used to manufacture cotton fabrics. Cellulose is used to make paper and cardboard, and by chemical processing—a great variety of products such as artificial fibre, plastics, varnishes, smokeless powder, and ethyl alcohol (see p. 152).

The most widespread industrial method of separating cellulose from wood consists in the treatment of wood pulp at an elevated temperature and pressure with a solution of calcium hydrogen sulphite $Ca(HSO_3)_2$. The wood decomposes, the lignin in it passes into solution, while the cellulose remains unchanged. Next the cellulose is separated from the solution, washed with water, dried, and delivered for further processing. The cellulose produced in this way is often called **sulphite cellulose**.

Cellulose does not dissolve in water, diethyl ether, and ethyl alcohol, it does not decompose under the influence of dilute acids, and is stable to the action of alkalis and weak oxidizing agents.

When treated in the cold with concentrated sulphuric acid, cellulose dissolves in it to form a viscous solution. If this solution is poured into an excess of water, a white flaky product is formed known as **amyloid**, which is partly hydrolyzed cellulose. It is similar to starch in its reaction with iodine (a blue colour; cellulose does not give this reaction). If unsized paper is dipped for a short time into concentrated sulphuric acid and then immediately rinsed, the amyloid thus formed cements the paper fibres together, making it denser and stronger. This is how **parchment paper** is made.

Upon the prolonged treatment of cellulose with concentrated solutions of mineral acids, it hydrolyzes when heated, the product being glucose.

Cellulose molecules contain alcohol hydroxyl groups: each glucose residue contains three such groups, and the formula of cellulose can be written as $[C_6H_7O_2(OH)_3]_x$. Consequently, both ethers and esters can be prepared from it.

The esters of cellulose and nitric acid—**cellulose nitrates** (**nitrocellulose**)—may have the composition $[C_6H_7O_2(OH)_2(ONO_2)]_x$.

$[\text{C}_6\text{H}_7\text{O}_2(\text{OH})(\text{ONO}_2)_2]_x$, and $[\text{C}_6\text{H}_7\text{O}_2(\text{ONO}_2)_3]_x$. They are used to produce smokeless powder (pyroxyline), celluloid, nitrolacquers, etc. The acetic acid esters of cellulose (**cellulose acetates**, or **acetyl cellulose**), for example $[\text{C}_6\text{H}_7\text{O}_2(\text{OCCCH}_3)_3]_x$, are used to produce incombustible photographic and cinema films, various transparent plastics, and lacquers.

Of great industrial significance is the chemical processing of cellulose into artificial fibre (p. 177).

Artificial fibre is produced from cellulose in three ways: by the viscose, acetate, and copper-ammonia methods.

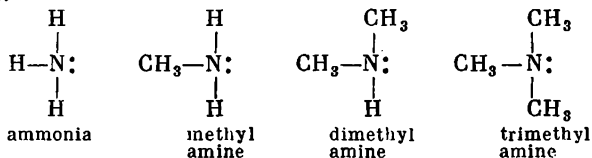
In the **viscose method**, cellulose is treated with sodium hydroxide, and then with carbon disulphide. The orange mass formed, referred to as **xanthogenate**, is dissolved in a weak solution of sodium hydroxide to produce **viscose**. The latter is forced through special caps with minute apertures (**spinnerets**) into a precipitation bath containing an aqueous solution of sulphuric acid. As a result of reacting with the sulphuric acid, the alkali is neutralized, and the viscose decomposes, detaching the carbon disulphide and forming lustrous threads of cellulose of a somewhat modified composition. These threads are **viscose fibre** (**viscose rayon**).

In the **acetate method**, a solution of cellulose acetate in acetone is forced through spinnerets towards a counterflow of warm air. The acetone evaporates, and the jets of the solution transform into very thin threads—**acetate fibre**.

A less widespread method is the **copper-ammonia** one in which a characteristic property of cellulose is used, namely, its ability to dissolve in an ammonia solution of copper(II) oxide, $[\text{Cu}(\text{NH}_3)_4](\text{OH})_2$ (Schweizer's reagent). The cellulose is again separated from this solution by acids. The fibre threads are produced by forcing the copper-ammonia solution through spinnerets into a precipitation bath containing an acid solution.

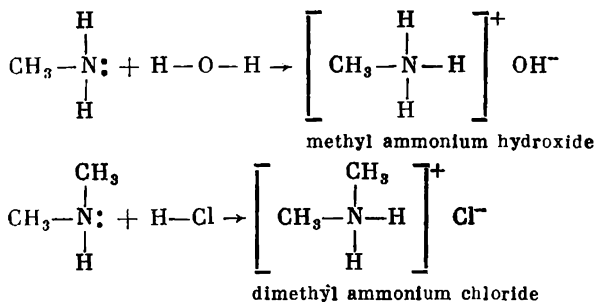
61. Amines

These organic compounds are derivatives of ammonia. They can be considered as the products of replacement of one, two, or all three hydrogen atoms in the ammonia molecule by hydrocarbon radicals:



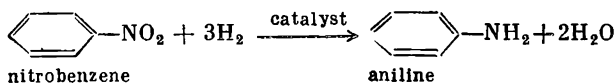
Amines are **organic bases**. At the expense of the free (unshared) pair of electrons belonging to the nitrogen atom, their molecules, like the ammonia one (Vol. 1, p. 135) can gain protons, detaching them for instance, from water or acid molecules. Amines form com-

plex hydroxides with water, and substituted ammonium salts with acid:



Amines of the fatty series containing simple hydrocarbon radicals are encountered in the products of protein decomposition.

Of great industrial significance are the aromatic amines containing aromatic hydrocarbon radicals. The most important of them is **aniline** $\text{C}_6\text{H}_5-\text{NH}_2$. It is prepared by reducing nitrobenzene in the presence of a catalyst:



This reaction was discovered in 1842 by N. Zinin and is known as the **Zinin reaction**. It is hard to overestimate the significance of this discovery. Aniline and other aromatic amines prepared in a similar way from various nitrocompounds are used in the production of numerous synthetic dyes, drugs, photographic reagents, plastics, explosives, and other valuable materials.



Nikolai Nikolayevich Zinin
(1812-1880)

Nikolai Nikolayevich Zinin, a prominent Russian chemist and the founder of the famous Kazan school of organic chemists, was born in 1812. His scientific and pedagogical activities were first associated with the Kazan University, where in 1842 he discovered the reaction of aniline preparation. A small amount of this substance prepared personally by Zinin has been carefully kept up to the present time at the chemical laboratory of the university. In 1847, Zinin moved to Petersburg, where he headed a department at the Academy of Medicine and

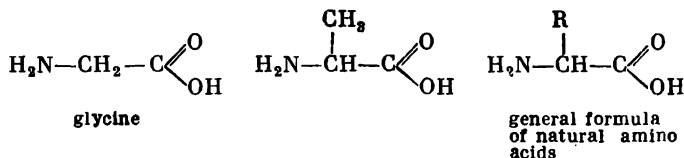
Surgery, and in 1865 he was elected a member of the Russian Academy of Sciences.

In addition to the synthesis of aniline, Zinin conducted a number of other organic syntheses that were of great practical significance.

Zinin was the first president of the Russian Chemical Society founded in 1868 (it is now the All-Union Mendeleev Chemical Society).

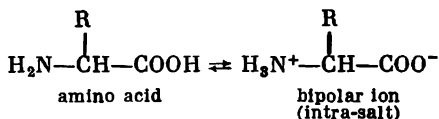
62. Amino Acids and Proteins

Of great biological significance are **amino acids**—compounds with mixed functional groups—which like amines contain amino groups —NH_2 and simultaneously, like acids, contain carboxyl groups —COOH . The simplest compounds exemplifying amino acids are **amino acetic acid**, or **glycine**, and **amino propionic acid**, or **alanine**. The structure of other natural amino acids of this type can be represented by the general formula given below (where R is a hydrocarbon radical that may also contain various functional groups):



Amino acids are amphoteric compounds: they form salts with bases (at the expense of the carboxyl group) and with acids (at the expense of the amino group).

The hydrogen ion detaching itself in dissociation from the carboxyl of an amino acid can transfer to its amino group with the formation of an ammonium grouping. Hence, amino acids also exist and enter into reactions in the form of **bipolar ions** (intra-salts):



This explains why solutions of amino acids containing one carboxyl and one amino group have a neutral reaction.

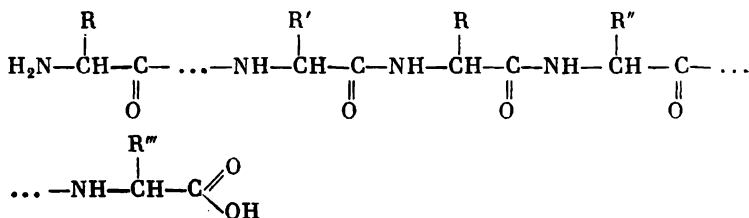
Molecules of **proteins** are built up of amino acids. Upon complete hydrolysis under the influence of mineral acids, alkalies, or enzymes, proteins decompose to form mixtures of aminoacids.

Proteins are natural high-molecular nitrogen-containing organic compounds. They play a paramount role in all vital processes and

are carriers of life. Proteins are contained in all the tissues of organisms, the blood, and the bones. Enzymes and many hormones are complex proteins. Skin, hair, wool, feathers, horns, hoofs, bones, and threads of natural silk are all formed by proteins. Proteins, like carbohydrates and fats, are a very important and essential constituent part of food.

Proteins include carbon, hydrogen, oxygen, nitrogen, and often sulphur, phosphorus, and iron. The molecular mass of proteins is very high, from 1500 to several millions.

The problem of the structure and synthesis of proteins is most important in today's science. Much has been achieved in this field in the last few decades. It has been established that tens, hundreds, and thousands of amino acids forming giant protein molecules combine with one another, liberating water at the expense of their carboxyl and amino groups. The structure of the chain of such a molecule can be represented as follows:



In protein molecules, the groups of atoms $-\text{CO}-\text{NH}-$ repeat many times. They are known as **amide**, or in the chemistry of proteins—**peptide groups**. Proteins are accordingly related to the natural high-molecular compounds **polyamides** or **polypeptides**.

The entire diversity of proteins is formed by 20 different amino acids. The sequence in which the residues of the amino acids forming a protein combine with one another is strictly specific for each protein. Methods have been found of establishing this sequence, and as a result, the structure of some proteins has been found exactly. And the most remarkable achievement in this field was the synthesis of the simplest proteins from amino acids. We have already indicated that in the fifties and sixties of the present century, the hormone insulin and the enzyme ribonuclease were prepared synthetically. Hence, the possibility in principle of synthesizing even more complex proteins has been proved.

63. Natural and Synthetic High-Molecular Compounds (Polymers)

High-molecular compounds, or **polymers**, are defined to be complex substances with large molecular masses (of the order of hundreds, thousands, and millions) whose molecules are built up of a multitude

of repeating **elementary units** formed as a result of the combination with one another of identical or different simple molecules—**monomers**.

The following two processes lead to the formation of high-molecular compounds: (a) a **polymerization reaction**—a process as a result of which molecules of a low-molecular compound (a monomer) combine with one another by means of covalent bonds to form a new substance (polymer) whose molecular mass is an integral number of times greater than that of the monomer; polymerization is characteristic chiefly of compounds with multiple (double or triple) bonds; (b) a **polycondensation reaction**—a process of formation of a polymer from low-molecular compounds containing two or more functional groups attended by the liberation of substances such as water, ammonia, and a hydrogen halide at the expense of these groups; the composition of an elementary unit of the polymer in this case differs from that of the initial monomer.

Examples of **natural high-molecular compounds** are starch and cellulose built up of elementary units that are the residues of a monosaccharide (glucose), and also proteins whose elementary units are amino acid residues; other examples are natural rubbers or caoutchoucs (see below).

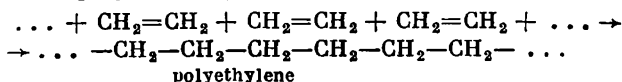
Synthetic high-molecular compounds or, as they are otherwise called, **synthetic high polymers**, are acquiring a greater and greater significance. They include a variety of materials usually prepared from an available and cheap starting material. They are the basis for the production of **plastics**—complex compositions into which various fillers and additions are introduced to impart the required collection of technical properties to the polymers, and also of synthetic fibres (see p. 177).

Polymers and plastics based on them are valuable substitutes for many natural materials (metals, wood, leather, glues, etc.). Synthetic fibres successfully compete with natural ones—silk, wool, and cotton. It is important to stress that in a number of properties materials based on synthetic polymers are often superior to natural ones. Plastics, fibres, and other compounds can be produced with a collection of preset technical properties. This makes it possible to solve many problems of modern engineering that could never have been solved with the use of only natural materials. The plans for the development of the USSR's national economy provide for the widespread and constantly growing development of the production of synthetic polymers and various materials based on them*.

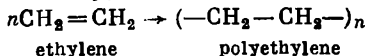
Polymerization Resins. These compounds include polymers prepared by the polymerization of mainly ethylene hydrocarbons or their derivatives.

* In 1977, the amount of plastics and synthetic resins produced in the Soviet Union was 3.3 million tonnes.

Polyethylene is a polymer formed in the polymerization of ethylene, for instance when it is compressed to 150-250 MPa at 150-250 °C (**high-pressure polyethylene**)



or, more briefly,

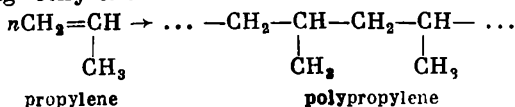


A polymerization reaction can be represented as the result of opening of the double bonds in a multitude of molecules of an unsaturated compound (ethylene in the given case) and the following combination of these molecules with one another into a single gigantic macromolecule. The quantity n is referred to as the **degree of polymerization**—it shows the number of monomer units forming a macromolecule. The polymerization of ethylene is initiated by introducing a small amount (0.05-0.1%) of oxygen.

Catalysts have been found that cause ethylene to polymerize at low pressures. For instance, in the presence of triethyl aluminium $(\text{C}_2\text{H}_5)_3\text{Al}$ with an addition of titanium(IV) chloride TiCl_4 (a Ziegler catalyst), polymerization occurs at atmospheric pressure (**low-pressure polyethylene** is produced); on chromium oxides (the Phillips catalyst) a polymer is formed at a pressure of up to 10 MPa (**medium-pressure polyethylene**).

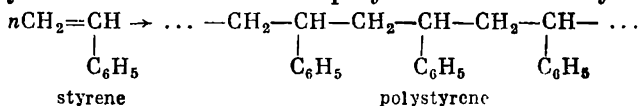
Polyethylene is a saturated hydrocarbon with a molecular mass ranging from 10 000 to 400 000. It is a wax-like but hard material melting at 110 to 125 °C, colourless and semitransparent in thin layers and white in thick ones. It has a high chemical stability, waterproofness, and a low gas permeability. It is used as an electrical insulating material, and also for making films employed as a packing material, for fabricating light-weight unbreakable plates and dishes, hoses and pipes for the chemical industry. The properties of polyethylene depend on how it was made; for example, high-pressure polyethylene has a lower density and a lower molecular mass (10 000 to 45 000) than its low-pressure counterpart (a molecular mass of 70 000 to 400 000), which affects its technical properties. Only high-pressure polyethylene may be used for contact with food products because low-pressure polyethylene may contain remnants of catalysts—heavy metal compounds that are harmful for a person's health.

Polypropylene is a polymer of propylene, the alkene homologue following ethylene:



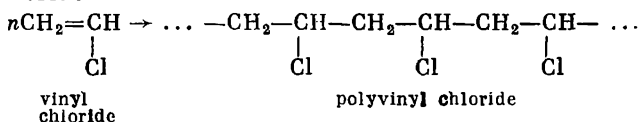
Polymerization occurs in the presence of catalysts. Depending on the polymerization conditions, polypropylene is prepared differing in the structure of its macromolecules, and, consequently, in its properties. In appearance, it is a rubber-like mass more or less hard and elastic. It differs from polyethylene in its higher melting point. For instance, polypropylene with a molecular mass above 80 000 melts at 174-175 °C. Polypropylene is used for electrical insulation, for making protective films, pipes, hoses, gear wheels, components of instruments, and also high-strength and chemically stable fibre. The latter is employed in the production of ropes, fishnets, and the like. Polypropylene films are considerably stronger and more transparent than polyethylene ones. Food products in a polypropylene packing can be sterilized, cooked, and warmed up.

Polystyrene is formed in the polymerization of styrene:



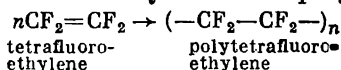
It can be obtained as a transparent vitreous mass. It is used as an organic glass, for the fabrication of consumer goods (buttons, combs, etc.), and as an electrical insulator.

Polyvinyl chloride (PVC) is produced by the polymerization of vinyl chloride:



It is an elastic mass, very stable to the action of acids and alkalis. It is widely used for lining pipes and vessels in the chemical industry. It is employed for insulating electrical conductors, making artificial leather, linoleum, and waterproof coats. The chlorination of polyvinyl chloride yields **perchlorovinyl resin** from which the chemically stable synthetic fibre **Chlorin** is prepared.

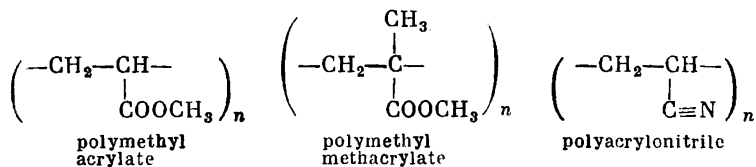
Polytetrafluoroethylene is a polymer of tetrafluoroethylene:



Polytetrafluoroethylene is produced in the form of plastics known as **Teflon** or **Fluoroplast**. It is very stable with respect to alkalis and concentrated acids, as well as to other reagents. It is superior to gold and platinum in its chemical stability. It is not combustible, and has high dielectrical properties. It is used in chemical and electrical engineering.

Polyacrylates and polyacrylonitrile. Of great importance are the polymers of the unsaturated **acrylic** $\text{CH}_2=\text{CH}-\text{COOH}$ and **methacrylic** $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOH}$ acids, especially of their methyl

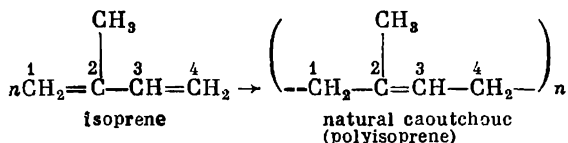
esters—**methyl acrylate** and **methyl methacrylate**, and also **acrylic acid nitrile** (or acrylonitrile) $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$, a derivative of this acid in which the carboxyl group $-\text{COOH}$ is replaced with the group $-\text{C}\equiv\text{N}$. The structure of the most important of these polymers is expressed by the formulas:



Polymethyl acrylate and polymethyl methacrylate are solid, colourless, transparent polymers that resist heating and the action of light and transmit ultraviolet rays. They are used to make sheets of strong and light-weight **organic glass** widely employed for various components. Polyacrylonitrile is used to produce **Nitron** (or **Orlon**)—synthetic fibres employed in the fabrication of knitted wear and fabrics (for clothing and technical needs).

Caoutchoucs (raw rubbers) are elastic materials from which commercial rubber is prepared by special treatment. Caoutchoucs are used in engineering to manufacture tyres for motor vehicles, aeroplanes, bicycles, for electrical insulation, and also for the production of consumer goods and medical instruments.

Natural caoutchouc is a high-molecular unsaturated hydrocarbon whose molecules contain a great number of double bonds; its composition can be expressed by the formula $(\text{C}_5\text{H}_8)_n$ (where the quantity n ranges from 1000 to 3000); it is a polymer of isoprene:

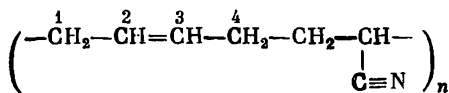


Examination of this equation shows that in the polymerization of isoprene both its double bonds open, while in an elementary unit of the polymer a double bond appears at a new site—between carbon atoms 2 and 3.

Natural caoutchouc is contained in the latex of rubber plants, chiefly tropical ones (for instance, the Brazilian tree hevea).

Another natural product—**gutta-percha**—is also a polymer of isoprene, but with a different configuration of its molecules.

Caoutchouc is sticky, weak, and becomes brittle when the temperature is lowered slightly. To impart the required strength and elasticity to articles made from it, caoutchouc is **vulcanized**—sulphur is introduced into it, and the mixture is then heated. The vulcanized product is called **rubber**.



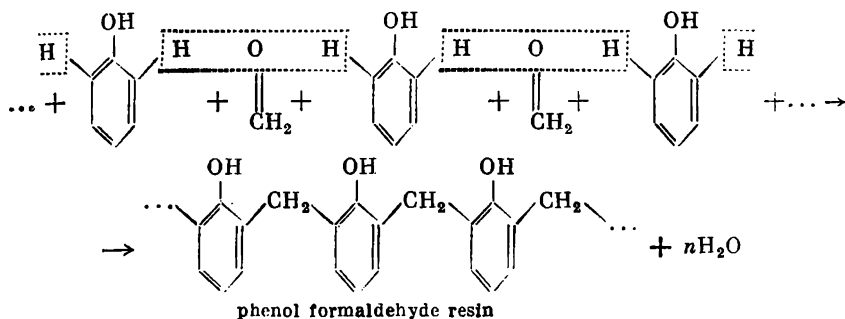
butadiene-nitrile rubber

In the molecules of these rubbers, the butadiene units alternate with the units of styrene and acrylonitrile, respectively.

The preparation of a synthetic polyisoprene rubber close in its properties to natural rubber has been developed in the USSR and is being introduced into production.

Condensation Resins. These resins include polymers prepared by a polycondensation reaction.

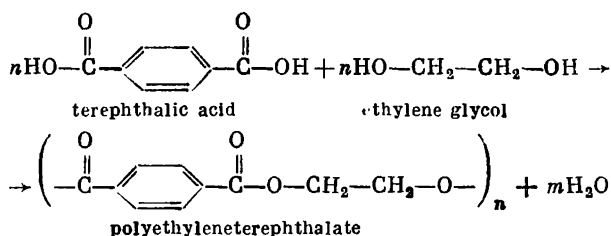
Phenol formaldehyde resins are high-molecular compounds formed owing to a reaction between phenol ($\text{C}_6\text{H}_5\text{OH}$) and formaldehyde ($\text{CH}_2=\text{O}$) in the presence of acids (HCl , etc.) or alkalis (NaOH , NH_4OH) as catalysts:



The process is attended by the liberation of water. Phenol formaldehyde resins have a remarkable property: when heated, they first become soft, while upon further heating (especially in the presence of the relevant catalysts) they harden. These resins are used to prepare valuable plastics—**phenolic plastics (phenoplasts)**. The resins are mixed with various fillers (wood flour, comminuted paper, asbestos, graphite, etc.), with plasticizers and dyes, and the resulting compound goes to prepare various articles by hot pressing techniques. Phenol formaldehyde resins have recently found new fields of application, for instance, in the production of building components from wood residues, and the manufacture of shell moulds in foundries.

Polyesters. An example of these compounds is the product of polycondensation of the dibasic aromatic terephthalic acid with

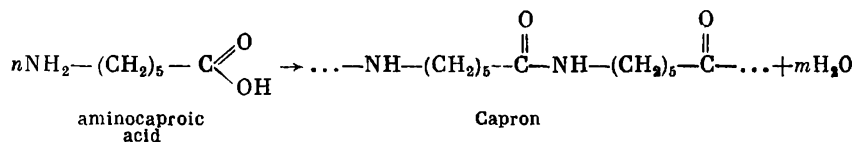
the diatomic alcohol ethylene glycol:



Polyethyleneterephthalate is a polymer in whose molecules an ester grouping repeats many times. In the USSR, this polyester is produced under the trade name **Lavsan** (in the United States it is known as **Dacron**, and in Western Europe as **Terylene**). It is used to manufacture fibres similar to wool, but considerably stronger and going to make non-wrinkling fabrics. Lavsan has a high resistance to heat, moisture, and light, and is stable against alkalis, acids, and oxidizers.

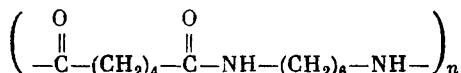
Polyamides. Polymers of this kind are synthetic analogues of proteins. Their chains contain repeating **amide** groups $-\text{CO}-\text{NH}-$ like those in proteins. In the chains of protein molecules, they are separated by a unit of one C-atom, and in synthetic polyamides—by a chain of four and more C-atoms. The fibres produced from synthetic polyamides—**Capron**, **Enant**, and **Anid**—are in some properties considerably superior to natural silk. In the textile industry, they are used to produce attractive and durable fabrics and knitted goods. In engineering, Capron or Anid strings and ropes are used because of their high strength; these polymers are also used for the cord of motor vehicle tyres, for making nets and various technical fabrics.

Capron (Nylon-6) is a polycondensate of aminocaproic acid containing a chain of six carbon atoms:



Enant is a polycondensate of aminoanthic acid containing a chain of seven carbon atoms.

Anid (Nylon-6,6 or Ferlon) is prepared by the polycondensation of the dibasic adipic acid $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$ and hexamethylene diamine $\text{NH}_2-(\text{CH}_2)_6-\text{NH}_2$. The structure of the Anid chain is:



Natural and Chemical Fibres. All textile fibres employed in the production of various kinds of yarn are divided into natural and chemical ones.

Natural fibres are formed in plants (cotton, linen, and other fibres consisting of cellulose) or from the secretions of living organisms (wool, silk threads secreted by the mulberry silkworm, consisting of proteins).

Chemical fibres include all the artificially produced ones. They are divided, in turn, into artificial fibres (for instance, rayon) produced in the chemical processing of natural substances (chiefly cellulose) and synthetic fibres produced from specially synthesized chemical materials (chiefly synthetic high-polymers).

The artificial fibres include those of viscose, acetate, and copper-ammonia silk produced by the processing of cellulose (p. 166). Examples of synthetic fibres are those considered above, which are produced from addition (Chlorin, Nitron) or condensation (Lavsan, Capron, Enant, Anid) polymers.

The production of chemical fibres is of a tremendous significance for the national economy. Its development improves the well-being of the people. It allows the constantly growing demand for consumer's goods such as various fabrics, knitted wear, and artificial furs to be met. In engineering, the existence of diverse chemical fibres with a definite collection of properties makes it possible to solve many important problems.

In 1977, 1088 thousand tonnes of chemical fibres were produced in the USSR.

SILICON (*SILICIUM*)

64. Occurrence. Preparation and Properties

Silicon is one of the most abundant elements in the Earth's crust. It forms 27% (mass) of the part of the Earth's crust accessible for investigation and occupies the second place, after oxygen, with respect to abundance.

Silicon is encountered in nature only in compounds: in the form of silicon dioxide SiO_2 , also known as silica, and of salts of silicic acids (silicates). The most widespread in nature are aluminosilicates, i.e. silicates containing aluminium. Among them are feldspars, micas, kaolin, etc.

In the same way as carbon, which is contained in all organic substances, is the most important element in the kingdom of plants and animals, so is silicon the chief element in the kingdom of minerals and rocks.

The content of silicon in most organisms is very insignificant. But some marine organisms accumulate large amounts of silicon.

Sea plants rich in it include Diatoma, among marine animals containing a lot of silicon are Radiolaria and silicon sponges.

Free silicon can be prepared by roasting fine white sand, which is silicon dioxide, with magnesium:



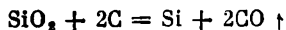
A brown powder of amorphous silicon is formed.

Silicon dissolves in molten metals. When a solution of silicon in zinc or in aluminium is slowly cooled, the silicon separates as well-formed octahedral crystals. Crystalline silicon has a steel lustre.

Highly pure silicon crystals having a minimum number of structural defects are characterized by a very low electrical conductivity. Impurities and violations of the regular structure sharply increase their conductivity.

Silicon is chiefly used in metallurgy and in semiconductor engineering. In metallurgy, it is employed for removing oxygen from molten metals and is a component of many alloys. The most important of them are alloys based on iron, copper, and aluminium. In semiconductor engineering, silicon is used in the manufacture of photoelectric cells, amplifiers, and rectifiers. Semiconductor devices based on silicon withstand heating to 250 °C, which broadens their sphere of application.

Silicon is produced commercially by reducing silicon dioxide in electrical furnaces:

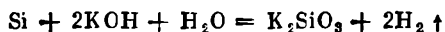


The silicon obtained in this way contains from 2 to 5% impurities. The high-purity silicon needed for the manufacture of semiconductor devices is produced in a more complicated way. Natural silica is converted to a silicon compound that lends itself to deep purification. Next the silicon is separated from the pure substance obtained by thermal decomposition or by the action of a reducing agent. One of these methods consists in converting silica to silicon chloride SiCl_4 , purifying this product, and reducing the silicon from it with the aid of highly pure zinc. Very pure silicon can also be produced by the thermal decomposition of silicon iodide SiI_4 or silane SiH_4 . The obtained silicon contains very little impurities and is suitable for manufacturing some semiconductor devices. To produce a still purer product, it is additionally purified, for example by zone refining (see Sec. 79).

In the chemical respect, silicon, especially the crystalline modification, has a low activity. At room temperature, it combines directly only with fluorine. When heated, amorphous silicon readily combines with oxygen, the halogens, and sulphur.

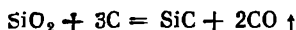
Acids, except for a mixture of hydrogen fluoride and nitric acid, do not react with silicon, but alkalis vigorously react with it,

liberating hydrogen and forming salts of silicic acid H_2SiO_3 :



In the presence of traces of an alkali playing the role of a catalyst, silicon also displaces hydrogen from water.

If a mixture of sand and coke taken in a definite proportion is heated in an electrical furnace, a compound of silicon with carbon is formed—silicon carbide SiC , called carborundum:

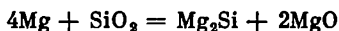


Pure carborundum is a colourless very hard crystalline substance (its density is 3.2 g/cm^3). The commercial product is usually coloured dark gray by impurities.

The internal structure of carborundum is like that of diamond in which half of the carbon atoms have been uniformly replaced with silicon atoms. Each carbon atom is at the centre of a tetrahedron at whose corners silicon atoms are located; each silicon atom, in turn, is surrounded in a similar way by four carbon atoms. The covalent bonds joining all the atoms in this structure, as in diamond, are very stable. This explains the great hardness of carborundum.

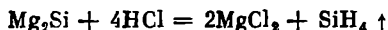
Carborundum is produced in large amounts. It has a variety of applications associated with its great hardness and refractoriness. Carborundum powder goes to make grinding wheels, whetstones, and carborundum cloth. Slabs for the construction of floors, platforms, and passages in underground railways and railway stations are made on its basis. It is used to manufacture muffles and linings for various furnaces and kilns. A mixture of carborundum and silicon powders is the material used to fabricate Silite rods for electrical furnaces.

At a high temperature, silicon combines with many metals to form silicides. For example, when silicon dioxide is heated with an excess amount of metallic magnesium, the reduced silicon combines with magnesium to form magnesium silicide Mg_2Si :

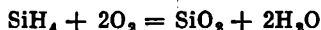


65. Compounds of Silicon with Hydrogen and the Halogens

The reaction of hydrogen chloride with magnesium silicide Mg_2Si yields silane SiH_4 , which is similar to methane:

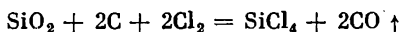


Silane SiH_4 is a colourless gas that self-ignites in air and burns with the formation of silicon dioxide and water:



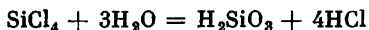
In addition to SiH_4 , several other hydrogen compounds of silicon are known that bear the common name **silanes**, for instance **disilane** Si_2H_6 and **trisilane** Si_3H_8 . The silanes are similar to the relevant alkanes, but are less stable. The bond between the silicon atoms is evidently much less stable than that between carbon atoms, and this is why the chains $-\text{Si}-\text{Si}-\text{Si}-$ are readily decomposed. The bond between silicon and hydrogen is also not stable, which points to the considerable weakening of the non-metallic properties in silicon.

Silicon tetrachloride SiCl_4 is produced by heating a mixture of silicon dioxide with coal in a stream of chlorine:



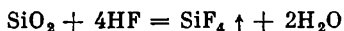
or by the chlorination of commercial silicon. It is a liquid boiling at 57°C .

Silicon tetrachloride becomes completely hydrolyzed in water and forms silicic and hydrochloric acids:



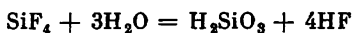
Owing to this reaction, a dense smoke is formed when SiCl_4 evaporates in humid air. Silicon tetrachloride is used to synthesize organo-silicon compounds.

Silicon tetrafluoride SiF_4 is formed when hydrogen fluoride reacts with silicon dioxide:



It is a colourless gas with a pungent odour.

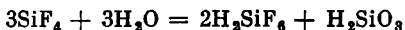
Like silicon tetrachloride, SiF_4 hydrolyzes in aqueous solutions:



The hydrogen fluoride thus formed reacts with the SiF_4 . The product is **fluosilicic** (or **silicofluoric**) acid H_2SiF_6 :



The complete process is expressed by the equation



The strength of fluosilicic acid is close to that of sulphuric acid. Its salts—**fluosilicates** (or **silicofluorides**) are mostly soluble in water. The salts of sodium, potassium, rubidium, and cesium are only slightly soluble, and the barium salt is virtually insoluble. *The acid itself and all the fluosilicates are poisonous.*

Sodium fluosilicate Na_2SiF_6 is used as an insecticide, and is also a component of mixtures for producing cements and enamels. The soluble fluosilicates of magnesium, zinc, and aluminium are used in construction. These substances make the surface of building stone such as limestone and marble waterproof, which is explained by the formation of poorly soluble fluorides and silica.

66. Silicon Dioxide

The most stable compound of silicon is **silicon dioxide**, or **silica**, SiO_2 . It occurs both in the crystalline and the amorphous form.

Crystalline silicon dioxide is chiefly found in nature as the mineral **quartz**. The transparent colourless crystals of quartz having the shape of hexagonal prisms with hexagonal pyramids on their ends are known as **rock crystal** (Fig. 30). Rock crystal coloured lilac by impurities is called **amethyst**, and coloured brownish is called **smoky topaz**. But quartz is most often encountered as continuous semitransparent bodies, colourless or of a variety of colours. **Flint** is a variety of quartz. The finely crystalline varieties include **agate** and **jasper**. Quartz is also a component of many complex rocks such as granite and gneiss.

Ordinary sand consists of fine quartz grains. Pure sand is white, but it is most often coloured yellow or reddish by iron compounds.

Crystalline silicon dioxide is very hard, insoluble in water, and melts at about 1610°C , transforming into a colourless liquid. Cooling of this liquid yields a transparent vitreous body of amorphous silicon dioxide similar in appearance to glass.

Amorphous silicon dioxide occurs in nature much less frequently than the crystalline compound. Deposits of fine porous amorphous silica called **tripoli**, **diatomite**, or **infusorian earth** are encountered on the bottom of seas and oceans. These deposits were formed from the SiO_2 contained in the organisms of *Diatoma* and certain infusoria.

Acids except for hydrogen fluoride do not act on silicon dioxide. Hydrogen fluoride readily reacts with it to form silicon fluoride and water (see p. 30).

Silica in the form of sand is widely employed in construction, in the manufacture of glass (see Sec. 68), ceramics (see Sec. 69), cement (see Sec. 70), and abrasives. A special field of application of quartz is associated with the circumstance that it can deform under the action of an electric field. This property of quartz crystals is utilized in sound-recording and sound-reproducing apparatus and for generating ultrasonic oscillations.

67. Silicic Acids and Their Salts

Silicon dioxide is an acid oxide. The silicic acids poorly soluble

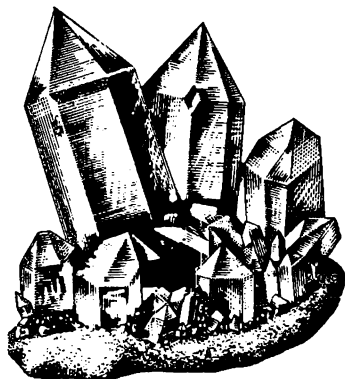
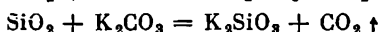
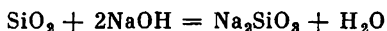


Fig. 30. Rock crystals

in water correspond to it. Their general formula is $n\text{SiO}_2 \cdot m\text{H}_2\text{O}$. Orthosilicic acid H_4SiO_4 , metasilicic (or silicic) acid H_2SiO_3 , and some other acids have been recovered in the free state. Metasilicic acid quite easily forms supersaturated solutions in which it gradually polymerizes and passes over into the colloidal state. Stable sols of silicic acid having a high concentration can be prepared with the aid of stabilizers. These solutions are used in certain production processes, for example in the manufacture of paper and for water treatment.

In the absence of stabilizers, the sol of silicic acid transforms into a gel. When the latter is dried, porous products (silica gels) are formed that are used as a drying agent (desiccant) and adsorbent.

The salts of silicic acids—silicates—are insoluble in water in the majority of cases; only sodium and potassium silicates are soluble. They are produced when silicon dioxide is melted with potassium and sodium hydroxides or carbonates, for instance:



Owing to their being similar in appearance to glass and to their solubility in water, sodium and potassium silicates are known as soluble glass.

Soluble glass in the form of aqueous solutions called water glass is used in the production of acid-resistant cement and concrete (see Sec. 70), for keroseneproof plasters over concrete, for impregnating fabrics, for preparing flameproof wood paints, and for the chemical stabilization of weak soils.

In solutions, Na_2SiO_3 and K_2SiO_3 are greatly hydrolyzed; these solutions have an alkaline reaction.

Silicates are exceedingly widespread in nature. We have already mentioned that the Earth's crust consists mainly of silica and various silicates. The natural silicates include feldspars, micas, clays, asbestos, talc, and many other minerals. Silicates are components of a large number of rocks such as granite, gneiss, basalt, and various schists. Many precious stones, for example, emerald, topaz, and aquamarine, are well-formed crystals of natural silicates.

The composition of natural silicates is generally expressed by quite complicated formulas. Owing to the complex nature of these formulas and also to the fact that the existence of the relevant polysilicic acids has not been proved, it is customary practice to write them somewhat differently than the ordinary formulas of salts.

The matter is that any salt of an oxyacid can be considered as a compound of an acid oxide with a basic one (or even with two basic oxides if the salt is a double one). For example, CaCO_3 can be considered as a compound of CaO and CO_2 , $\text{Al}_2(\text{SO}_4)_3$ as a compound of Al_2O_3 and 3SO_3 , and so on. This is why, when representing the com-

position of silicates, the formulas of silicon dioxide and all the oxides forming the silicate are usually written separately and joined by dots.

Below are given the formulas of some natural silicates:

Kaolin $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ or $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$

White mica $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ or $\text{H}_4\text{K}_2\text{Al}_6\text{Si}_6\text{O}_{24}$

Asbestos $\text{CaO} \cdot 3\text{MgO} \cdot 4\text{SiO}_2$ or $\text{CaMg}_3\text{Si}_4\text{O}_{12}$

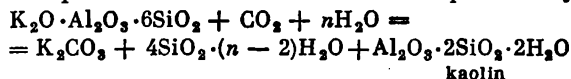
We have already mentioned that silicates containing aluminium are referred to as **aluminosilicates**. The most important of them are **feldspars**.

Feldspars, in addition to silicon and aluminium oxides, include oxides of potassium, sodium, or calcium. Common feldspar, or **orthoclase**, contains potassium oxide. Its composition is expressed by the formula $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. The predominating colour of feldspars is white or red. Feldspars are encountered in nature both as continuous deposits and as constituents of complex rocks.

Aluminosilicates also include **micas** distinguished by their ability to split into thin flexible flakes. Micas have a complex composition and in addition to silicon and aluminium contain hydrogen, potassium, or sodium; some micas also include calcium, magnesium, and iron. Ordinary white mica, whose large transparent sheets owing to their refractoriness are often used to close openings in various furnaces and kilns, is a potassium and aluminium silicate. Micas containing a large amount of iron and magnesium are black. Micas are not often encountered separately, but many rocks contain them. The most widespread complex rocks—**granites** and **gneisses**, consist of minute crystals of quartz, feldspar, and micas.

Minerals and rocks on the Earth's surface, coming into contact with the atmosphere and being subjected to the mechanical and chemical action of water and air, gradually change and break down. This destruction is called **erosion**. For example, water containing carbon dioxide acts on orthoclase so that K_2O detaches and combines with CO_2 to produce potash K_2CO_3 . Part of the SiO_2 also detaches, while the residue combines with water and forms a new silicate—**kaolin**, which is the basis of various **clays**.

The decomposition of orthoclase can be expressed by the equation:



Pure kaolin occurs comparatively rarely. It is coloured white and contains only an insignificant impurity of quartz sand. Such kaolin is used for the manufacture of porcelain. Ordinary clay is a mixture of kaolin with other substances imparting a yellowish brown or bluish colour to it.

Silicon compounds play an important role in the national economy. The applications of silicon dioxide were treated in the preceding

section. A number of silicate rocks, for instance, granites, are used as building materials. Silicates are the starting materials in the production of glass, ceramics, and cement (see the following sections). Mica and asbestos are used as electrical and thermal insulation. Silicates are used to make fillers for paper, rubber, and paints.

Some aluminosilicates have a porous structure and are capable of ion exchange. Such silicates—natural and especially artificial ones—are used for softening water (see Sec. 98). In addition, owing to their greatly developed surface, they are used as catalyst supports, i.e. as materials impregnated with a catalyst.

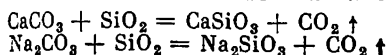
68. Glass

When mixtures of many silicates with other silicates or with silicon dioxide are heated, transparent amorphous products of fusion called **glasses** are produced.

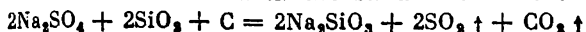
As regards their structure, glasses are supercooled systems. The cations and anions of the substance forming a glass are arranged relative to one another as in a liquid, i.e. with the observance of only close-range order (see Vol. 1, Sec. 53). At the same time, the nature of the motion of ions in glasses—mainly oscillations—is characteristic of the solid state. This structure is reflected in that unlike substances in the crystalline state, glasses do not have exact melting and freezing points. When heated, a glass softens, gradually transferring to the liquid state. When a molten glass is cooled, solidification also occurs gradually.

Glass was known to mankind from ancient times. But during many centuries, it was used only for manufacturing window glass and vessels. At present, glasses are produced having a variety of properties, and they are used for different purposes. Different starting materials are used to manufacture glasses with definite properties. In addition, the properties of glasses depend on the technology followed in their production.

Ordinary **window glass**, as well as the glass used to make the major part of domestic glassware (bottles, jars, glasses, etc.), consists chiefly of sodium and calcium silicates fused with silicon dioxide. The composition of such a glass is approximately expressed by the formula $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$. The starting materials for its production are white sand, soda, and lime or chalk. The following reactions occur when a mixture of these substances is fused:



Sodium sulphate Na_2SO_4 and coal are often used instead of soda. The coal reduces the sodium sulphate to sodium sulphite Na_2SO_3 that enters into a reaction with the sand to form sodium silicate:



If soda is replaced with potash in melting glass, refractory glass is produced. It is used for manufacturing vessels capable of withstanding strong heating.

When silicon dioxide is melted with potash and lead oxide, a heavy glass called **crystal** or **flint glass** is produced. It contains potassium and lead silicates. This glass has a high refractive index and acquires a high lustre when polished. It is used to make optical glasses and high-quality tableware.

The properties of glass are greatly affected by replacing part of the SiO_2 with boric anhydride B_2O_3 . The addition of the latter improves the hardness of the glass, increases its resistance to chemical action, and lowers its sensitivity to sharp temperature changes. This glass is used to produce high-quality chemical glassware.

Glass is customarily listed among the substances that are insoluble in water. Upon the prolonged action of water on ordinary glass, however, the water extracts some sodium silicate from it. If, for example, we shake powdered glass with water and then add a few drops of phenolphthalein to it, the liquid acquires a pink colour, which indicates an alkaline reaction (owing to the hydrolysis of the Na_2SiO_3).

In addition to the kinds of glass listed above, of great significance is the glass produced directly from quartz melted in an electrical furnace.

Quartz glass can withstand higher temperatures than ordinary glass. It transmits ultraviolet rays, which are retained by ordinary glass. A very valuable property of quartz glass is its exceedingly low coefficient of thermal expansion. This signifies that the volume of quartz glass remains almost unchanged when it is heated or cooled. Consequently, articles made from it can be greatly heated and then immersed in cold water: they do not crack.

Quartz glass is employed for making laboratory vessels and in the chemical industry. It is also used for making mercury-arc lamps whose light contains a lot of ultraviolet rays. These lamps find many applications in medicine, for scientific purposes, and in filming motion pictures. The shortcomings of quartz glass include the difficulty of working it and its brittleness.

Molten glass can be drawn through fine orifices (spinnarets) to produce filaments from 2 to 10 micrometres in diameter—**glass fibre**. It is not brittle and has a very high tensile strength. Fabrics from this fibre are non-flammable, have thermal, electrical and sound insulating properties, and are chemically stable.

The valuable properties of the materials manufactured from glass fibre underly their widespread use in various fields of engineering. Of great importance here are the availability and low cost of the basic starting material and the comparative simplicity of producing the glass fibre.

New building materials known as **glass fibre laminates** are produced by combining glass fibre with various synthetic resins. Their weight is from one-third to one-fourth that of steel, but they are not inferior to it in strength. This allows them to be used with great success as substitutes of both steel and wood. Glass fibre laminates are used, for example, to manufacture pipes withstanding a high hydraulic pressure and not subjected to corrosion. Glass fibre laminates are finding ever growing application in the motor vehicle, aviation, and ship-building industries.

The vitreous state of a substance is thermodynamically unstable. Glasses exist only because the viscosity grows very rapidly when molten glass is cooled so that crystallization has no time to occur. By introducing additions accelerating crystallization into the starting substances and conducting the melting process in definite conditions, it is possible to obtain crystalline glass materials known as **glass-ceramics, Sitalls, or Pyrocerams**.

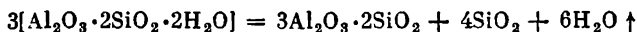
As regards their structure, Sitalls are fine crystals fused together by films of uncrystallized glass. They have a high strength, hardness, chemical and thermal stability. Sitalls belong to insulators with respect to their electrical properties. They can be used to make cheap and strong building materials, electrical insulators, radio components, and apparatus for chemical production processes

69. Ceramics

The name ceramics includes materials and articles made from refractory substances such as clay, and the carbides and oxides of certain metals. Depending on their application, there are distinguished building, refractory, chemically stable, domestic, and technical ceramics. Building ceramics includes brick, roofing and facing tiles, pipes and tubes. Refractory ceramics is used for the internal lining of various furnaces, for instance blast, steel-making, and glass furnaces. Chemically stable ceramics resists the action of chemically aggressive media not only at room, but also at elevated temperatures. It is used in the chemical industry. Domestic ceramics includes faience and porcelain articles. Technical ceramics is used to make insulators, capacitors, motor vehicle and aircraft spark plugs, high-temperature crucibles, and thermocouple tubes.

The process of manufacturing ceramic articles consists in preparing the ceramic mass, moulding, drying, and roasting. These operations are conducted differently depending on the nature of the starting materials and on the requirements which the product must meet. For example, in manufacturing bricks, the raw material—clay with additions of other minerals—is comminuted, mixed, and moistened. The plastic dough obtained is moulded, dried, and roasted (usually at 900 °C). In roasting (also known as firing, baking, and calcination),

sintering occurs owing to the chemical reactions in the solid phase. Sintering is conducted in strictly definite conditions and results in the production of a material having the preset properties. The basic reaction occurring in the roasting of clay can be schematically represented by the equation:



Some ceramic articles are coated with a **glaze**—a thin layer of a vitreous material. For this purpose, the article with a layer of powder consisting of quartz, feldspar, and certain additions applied to it is roasted again. The glaze makes a ceramic article waterproof, protects it from dirt, acids and alkalies, and imparts a lustre to it.

70. Cement

The most important materials manufactured by the silicate industry include **cement**, which is used in enormous amounts in construction work.

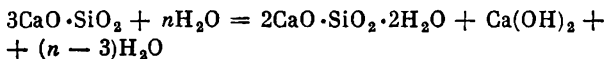
Ordinary cement (**silicate cement**) is produced by roasting a mixture of clay and limestone. In roasting of the cement mixture, the calcium carbonate decomposes into carbon dioxide and calcium oxide; the latter reacts with the clay to yield calcium silicates and aluminates.

The cement mixture is generally prepared artificially. But limestone and clay rocks called **marls** are sometimes encountered in nature whose composition is exactly that of a cement mixture.

The chemical composition of cements is customarily expressed in percentages of the oxides contained in them, the main ones of which are CaO , Al_2O_3 , SiO_2 , and Fe_2O_3 .

When silicate cement is mixed with water, a dough is obtained that hardens after some time elapses. The transition from the doughy state to the hard one is called "setting".

Cement sets in three steps. The first one consists in the reaction of the surface layers of the cement particles with water as follows:



Calcium hydroxide separates in the amorphous state from the solution contained in the cement dough, envelops the cement grains, and transforms them into a bound mass. This forms the second step—setting proper of the cement. Next, the third step begins—crystallization or hardening. The calcium hydroxide particles consolidate and transform into long needle-shaped crystals that make the calcium silicate mass more compact. This is attended by a growth in the mechanical strength of the cement.

When cement is used as a binder, it is usually mixed with sand and water. This mixture is known as **cement mortar**.

Concrete is prepared by mixing cement mortar with gravel or crushed stone. Concrete is an important building material. It is used to erect vaults, arches, bridges, reservoirs, residential buildings, etc. Structures made from concrete containing a carcass of iron or steel beams or bars are called **reinforced-concrete** ones.

Only a small amount of cement was produced in tsarist Russia. After the October Revolution, the constantly growing demand of the national economy for building materials resulted in a considerable growth in the cement industry, which was speeded up during recent years in connection with the broad program of industrial and residential construction. This is illustrated by the following figures:

Year	1913	1940	1953	1977
Cement produced, million tonnes	1.8	5.7	16.0	127

In addition to silicate cement, other kinds of cement are produced, particularly alumina and acid-resistant cements.

Alumina cement is produced by fusing a finely ground mixture of bauxite (a natural aluminium oxide) with limestone. The fraction of aluminium oxide contained in this cement is greater than in silicate cement. Its main components are various calcium aluminates. Alumina cement hardens much more rapidly than silicate cement. In addition, it resists the action of sea water more effectively. Alumina cement is much more expensive than its silicate counterpart, and for this reason it is used in construction only in special cases.

Acid-resistant cement is a mixture of finely ground quartz sand and an "active" silica substance having a highly developed surface. This substance is either tripoli first subjected to chemical treatment, or artificially produced silicon dioxide. After a solution of sodium silicate is added to the above mixture, a plastic dough is obtained that transforms into a stable mass resisting all acids except for hydrogen fluoride.

Acid-resistant cement is mainly used as a binder in the lining of chemical apparatus with acid-resistant tiles. It is sometimes used instead of the more costly lead.

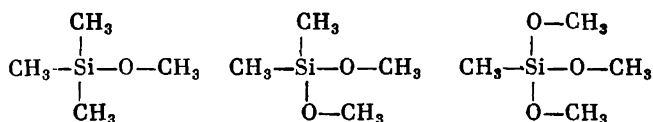
71. Organosilicon Compounds

A great number of silicon compounds are known in which the silicon atoms are chemically bonded to carbon atoms. They are called **organosilicons**.

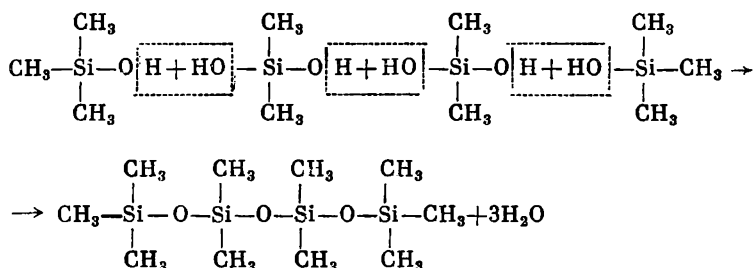
In 1936, the Soviet scientist K. Andrianov developed a method of synthesizing high-molecular organosilicon compounds that is now

the basis of an industrial process for the manufacture of a number of products having valuable properties.

Andrianov synthesized esters of derivatives of orthosilicic acid $\text{Si}(\text{OH})_4$ in which one, two, or three hydroxyl groups were replaced by hydrocarbon radicals, for example:



Hydrolysis of these esters ought to produce the corresponding hydroxyl-containing compounds of silicon, but they immediately condense with the detachment of water molecules and the formation of polycondensates. For instance, the substances produced in the hydrolysis of the mixture of $(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2$ and $(\text{CH}_3)_3\text{SiOCH}_3$ can further condense as follows:



With a small degree of condensation (if the molecules contain about ten silicon atoms), the products are liquids used as lubricating oils. Their valuable properties include the insignificant change in the viscosity within a broad temperature interval, and their chemical stability. In comparison with conventional lubricants, which are mixtures of saturated hydrocarbons, they are considerably more resistant to high temperatures.

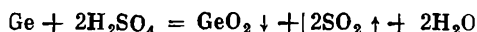
A higher degree of condensation results in products of a resinous nature. Owing to the high strength of the $\text{Si}-\text{O}$ bond, such resins have a high resistance to heating. They are also excellent electrical insulators and are employed to insulate conductors where conventional insulation may be rapidly destroyed as a result of the high temperature. Organosilicon resins are used to produce rubbery materials that retain their elasticity at temperatures from -60 to $+200^\circ\text{C}$ and are not destroyed even at 300°C .

Organosilicon compounds are used to waterproof glass, paper, fabrics, and building materials.

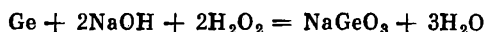
GERMANIUM, TIN, LEAD**72. Germanium**

This element, whose existence was predicted in 1871 by D. Mendeleev on the basis of his periodic law, was discovered in 1886 by the German chemist C. Winkler (see Vol. 1, p. 56). The total content of germanium in the Earth's crust is about 0.0007% (mass). Minerals containing considerable amounts of germanium are extremely rare. It is usually produced from the by-products obtained in processing non-ferrous metal ores, and also from the ash remaining when certain grades of coal are burned.

In a compact state, germanium has a silver colour and is similar in appearance to a metal. At room temperature, it is stable to the action of air, oxygen, water, hydrochloric and dilute sulphuric acids. Nitric and concentrated sulphuric acids oxidize it to the dioxide GeO_2 , especially when heated:



Germanium also reacts with alkalis in the presence of hydrogen peroxide to form salts of germanic acid—germanates. For instance:



Compounds of germanium(II) have a low stability. Much more characteristic of germanium are its compounds in which its oxidation number is +4.

Germanium dioxide GeO_2 forms white crystals having a density of 4.703 g/cm³ appreciably soluble in water, the solution conducting an electric current. The dioxide is produced in various ways, for instance, it can be prepared by heating germanium in oxygen or by oxidizing it with concentrated nitric acid.

Germanium dioxide is an amphoteric compound with greatly predominating acid properties. As a result, it can readily dissolve in alkalis to form germanates.

Germanium Hydrides. Germanium tetrahydride GeH_4 can be prepared by reacting germanium tetrachloride GeCl_4 with sodium amalgam in a stream of hydrogen or by decomposing an alloy of germanium with magnesium by means of acids. It is a colourless gas which, like arsenic hydride, decomposes when heated and forms a metallic mirror on the walls of the reaction vessel.

In the preparation of the simplest germanium hydride, a small amount of its homologues Ge_2H_6 and Ge_3H_8 are formed.

Germanium has semiconductor properties, and this underlies its chief application. The germanium used to manufacture semiconductor devices is subjected to very thorough purification. This is done in various ways. One of the most important of them is zone melting (see Sec. 79). To impart the required semiconductor properties to the puri-

fied germanium, a very small amount of definite impurities is introduced into it. They include elements of Groups five and three of the periodic table, for example, arsenic, antimony, aluminium, and gallium. Semiconductor equipment based on germanium (rectifiers, amplifiers) are widely used in radio and television engineering, in radar and computer equipment. Germanium is also used to make resistance thermometers.

Of the germanium compounds, mention must be made, for example, of GeO_2 , which is included in the composition of glasses having a high refractive index in the infrared part of the spectrum.

73. Tin (*Stannum*)

Tin does not belong to the widespread metals (its content in the Earth's crust is 0.04%), but it is readily extracted from its ores. This is why it was known to man in the form of its alloys with copper (bronze) back in ancient times. Tin is usually encountered in the form of its oxygen compound SnO_2 known as cassiterite or tinstone. It is produced from the latter by reduction with coal.

Tin in the free state is a silvery-white soft metal. When a tin rod is bent, a characteristic crackling noise is heard due to friction between the individual crystals. Tin is soft and ductile and can easily be rolled into thin sheets called **tin foil**.

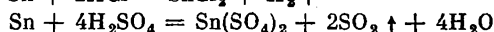
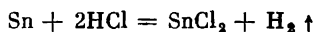
In addition to the ordinary **white tin** crystallizing in the tetragonal system, there is another modification—**gray tin**—that crystallizes in the cubic system and has a lower density. White tin is stable at temperatures above 14°C , and gray tin below this temperature. Hence, when white tin is cooled, it transforms into gray tin. In connection with the considerable change in the density of the metal attending this transition, it spills out in the form of a gray powder. This phenomenon was called **tin plague**. The rate of this transition of white tin into the gray modification is the highest at a temperature of about -30°C ; it becomes still higher in the presence of seeds of gray tin crystals.

Alloys of tin with antimony and copper are used in the manufacture of bearings. These alloys (tin Babbitt metals) have high anti-friction properties. Alloys of tin with lead—**solders**—are widely used in soldering. Tin is included as an alloying element in some copper alloys.

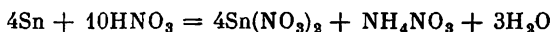
Tin does not oxidize in the air at room temperature, but when heated to above its melting point, it gradually transforms into tin dioxide SnO_2 .

Water does not react with tin. Dilute hydrochloric and sulphuric acids react with it very slowly, which is explained by the large over-voltage of hydrogen liberation on this metal. Concentrated solutions of the above acids, especially when heated, dissolve tin. Tin(II

chloride is obtained in hydrochloric acid, and tin(IV) sulphate in sulphuric acid:



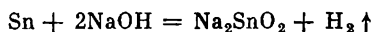
Tin reacts with nitric acid the more vigorously, the higher are the concentration of the acid and the temperature. In dilute acid, soluble tin(II) nitrate is formed:



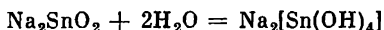
and in concentrated acid—compounds of tin(IV), chiefly insoluble **beta-stannic acid** whose composition approximately corresponds to the formula H_2SnO_3 :



Concentrated alkalis also dissolve tin. In this case, **stannites** are produced—salts of **stannous acid** H_2SnO_2 :



In solutions, stannites exist in hydrated forms producing **hydroxostannites**, for instance:

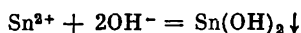


In air, tin becomes covered with a thin oxide film having a protecting action. Therefore, in conditions of a moderate corrosive action, it is a chemically stable metal. About 40% of all the tin produced is employed for coating iron articles coming into contact with food products, primarily cans. This is explained by the above-mentioned chemical stability of tin, and also by the fact that it is easily applied to iron and that the products of its corrosion are harmless.

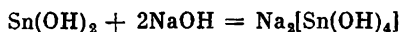
Tin forms stable compounds in which it has the oxidation number +2 or +4.

Compounds of Tin(II). *Tin(II) oxide* SnO is a dark brown powder formed when tin(II) hydroxide $\text{Sn}(\text{OH})_2$ decomposes in an atmosphere of carbon dioxide.

Tin(II) hydroxide $\text{Sn}(\text{OH})_2$ is produced in the form of a white precipitate when alkalis react with a salt of tin(II):



Tin(II) hydroxide is an amphoteric compound. It readily dissolves in both acids and alkalis, in the latter case with the formation of hydroxostannites:



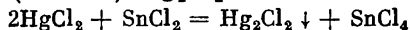
Tin(II) chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ forms colourless crystals. When tin(II) chloride is heated or greatly diluted with water, it partly hydrolyzes with the formation of a precipitate of the basic salt:



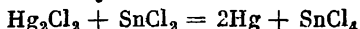
Tin(II) chloride is a reducing agent. For instance, it reduces iron(III) chloride FeCl_3 to iron(II) chloride FeCl_2 :



When tin(II) chloride reacts with a solution of mercury(II) chloride (corrosive sublimate) HgCl_2 , a white precipitate of mercury(I) chloride (calomel) Hg_2Cl_2 is formed:



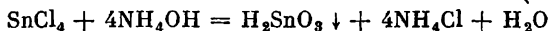
With excess tin(II) chloride, reduction proceeds even further, and metallic mercury is obtained:



Compounds of Tin(IV). *Tin dioxide* SnO_2 is encountered in nature and can be prepared artificially by burning the metal in air or by oxidizing it with nitric acid and then roasting the product. Tin dioxide is used to prepare white glazes and enamels.

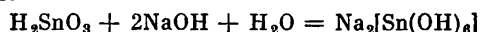
Tin(IV) hydroxides are called stannic acids and are known in two modifications: alpha-stannic acid and beta-stannic acid.

Alpha-stannic acid H_2SnO_3 can be prepared by the action of an aqueous solution of ammonia on a solution of tin(IV) chloride:



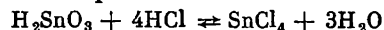
The white precipitate when dried gradually loses water and transforms into tin dioxide. Hence, an acid of a definite composition cannot be obtained. This is why the formula of alpha-stannic acid given above is only the simplest of the possible ones. It would be more correct to depict the composition of this acid by the formula $m\text{SnO}_2 \cdot n\text{H}_2\text{O}$.

Alpha-stannic acid is easily dissolved in alkalis to form salts containing the complex anion $[\text{Sn}(\text{OH})_6]^{2-}$ and known as **hydroxostannates**:



Sodium hydroxostannate separates from solutions in the form of crystals whose composition can be expressed by the formula $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$. This salt is used as a mordant in dyeing and as a filler for silk. Silk fabrics treated before dyeing with solutions of tin compounds sometimes contain up to 50% (mass) of tin.

Acids also dissolve alpha-stannic acid with the formation of tin(IV) salts. An example is:



When there is an excess of hydrogen chloride, tin(IV) tetrachloride adds two molecules of hydrogen chloride to form the complex **chlorostannic acid** $\text{H}_2[\text{SnCl}_6]$. The ammonium salt of this acid $(\text{NH}_4)_2[\text{SnCl}_6]$ has the same application as sodium hydroxostannate.

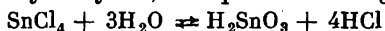
Beta-stannic acid is produced in the form of a white powder when concentrated nitric acid reacts with tin (see above). Its composition is just as indefinite as that of alpha-stannic acid. Unlike the latter,

it does not dissolve in acids or in solutions of alkalies. But by fusion with alkalies, it can be transferred into a solution in the form of a stannate. Alpha-stannic acid when stored in contact with the solution from which it was recovered also gradually transforms into beta-stannic acid.

Tin(IV) chloride or *tin tetrachloride* SnCl_4 is a liquid boiling at 112°C and strongly fuming in air. Tin(IV) chloride is formed when chlorine reacts with metallic tin or with tin(II) chloride. It is produced on a commercial scale chiefly by treating discarded tin plate (old tin cans) with chlorine.

Tin(IV) chloride dissolves in water and can be separated from a solution in the form of various crystal hydrates, for instance $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$.

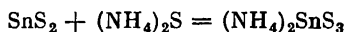
In aqueous solutions, especially in dilute ones, tin(IV) chloride becomes hydrolyzed, the product being alpha-stannic acid:



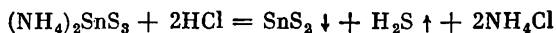
Tin(IV) hydride or *stannane* SnH_4 is a colourless, very poisonous gas. It liquefies at -52°C , while at room temperature it gradually decomposes into tin and hydrogen.

Tin Sulphides. When hydrogen sulphide reacts with a solution of tin(II) chloride, a brown precipitate of **tin(II) sulphide** SnS is obtained. In the same conditions, a yellow precipitate of **tin disulphide** [or **tin(IV) sulphide**] SnS_2 is obtained from a solution of tin(IV) chloride. Tin disulphide can also be prepared by heating tin shavings with sulphur and ammonium chloride. The disulphide obtained in this way has the form of golden yellow scales, and under the name of "gold tinsel" is used to gild wood.

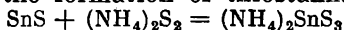
Tin disulphide dissolves in solutions of alkali metal and ammonium sulphides, the product being readily soluble salts of **thiostannic acid** H_2SnS_3 :



Free thiostannic acid is unknown. When acids act on its salts (**thiostannates**), hydrogen sulphide is liberated, and tin disulphide is obtained again:



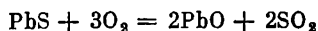
Tin(II) sulphide does not dissolve in alkali metal and ammonium sulphides, but ammonium and alkali metal polysulphides dissolve it with the formation of thiostannates:



74. Lead (*Plumbum*)

The lead content in the Earth's crust is 0.0016% (mass). The most important ore from which lead is extracted is **lead glance** or **galenite** PbS .

The first metallurgical operation in producing lead is roasting, during which the lead sulphide transforms into the oxide:



The lead(II) oxide obtained is melted in a mixture with coke, the product being black lead. It contains admixtures of many metals and is subjected to further purification.

Lead is a bluish-white heavy metal. It is very soft and can be cut with a knife.

Lead is widely used in engineering. The greatest amount of it goes to make cable sheathing and accumulator plates. At sulphuric acid plants, lead is used to make the housings of the towers, the coils of the coolers, and other important components of the apparatus. Lead goes to make ammunition and shot. It is included in many alloys, for example bearing alloys, type metal, and solders. Lead is a good absorber of gamma radiation and is used for protection from the latter when working with radioactive substances.

A certain amount of lead is used in the production of tetraethyl lead (see p. 141).

In air, lead rapidly becomes coated with a thin film of oxide that protects it from further oxidation. Water by itself does not react with lead, but in the presence of air lead is gradually destroyed by water with the formation of lead(II) hydroxide:

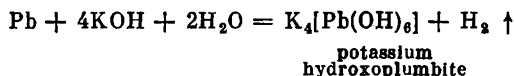


When it comes into contact with hard water, however, lead becomes covered with a protective film of insoluble salts (chiefly lead sulphate and basic lead carbonate) that prevents the further action of the water and the formation of the hydroxide.

Dilute hydrochloric and sulphuric acids almost do not react with lead. This is associated with the considerable overvoltage of hydrogen liberation on lead, and with the low solubility of lead chloride and sulphate that cover the surface of the dissolving metal. In concentrated sulphuric acid, especially when heated, lead vigorously dissolves with the formation of the soluble acid salt $\text{Pb}(\text{HSO}_4)_2$.

Lead dissolves readily in nitric acid, and at a higher rate in an acid having a moderate concentration than in a concentrated acid. The explanation is that the solubility of the corrosion product—lead nitrate—diminishes with an increase in the acid concentration. Lead dissolves comparatively easily in acetic acid containing dissolved oxygen.

Lead also dissolves in alkalis, although at a low rate; dissolving is more vigorous in hot dilute solutions. The products are hydroxoplumbites, for instance:

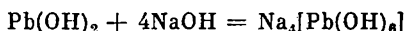


All soluble compounds of lead are poisonous.

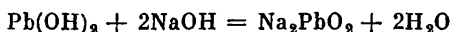
Lead is characterized by the oxidation numbers +2 and +4. The compounds with the oxidation number +2 are considerably more stable and numerous.

Compounds of Lead(II). *Lead(II) oxide* PbO is a yellow powder formed when molten lead is heated in air. After roasting at about 500 °C, it acquires a reddish-yellow colour, and in this form is known as **litharge**. Lead(II) oxide is used for filling the cells in accumulator plates and in the production of certain grades of glass, it is also the starting material for preparing other lead compounds.

Lead(II) hydroxide Pb(OH)₂ is formed when alkalis react with soluble salts of lead(II). It has amphoteric properties and dissolves in acids with the formation of salts of lead(II), and in alkalis with the formation of hydroxoplumbites, for instance:



When Pb(OH)₂ is fused with dry alkalis, salts called **plumbites** are obtained:



sodium
plumbite

Lead(II) chloride PbCl₂ is produced in the form of a white precipitate when solutions of lead(II) salts are reacted with hydrogen chloride or soluble chlorides. Lead(II) chloride is only slightly soluble in cold water, but its solubility grows greatly with elevation of the temperature.

Lead(II) iodide PbI₂ settles as a yellow precipitate from solutions of lead(II) salts when iodide ions are introduced into them. It is virtually insoluble in cold water, but dissolves well in hot water to form a colourless solution. When the latter is cooled, the lead(II) iodide precipitates in the form of golden yellow crystals.

Lead(II) acetate Pb(CH₃COO)₂ is among the few well soluble salts of lead widely used in laboratory practice. Lead(II) acetate has a sweet taste and is also known as **lead sugar**. It is used to dye fabrics and to produce other lead compounds.

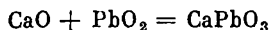
Lead(II) sulphate PbSO₄ settles as a white precipitate when sulphuric acid or soluble sulphates are added to solutions of lead(II) salts. Lead(II) sulphate is almost insoluble in water and in dilute acids, but dissolves quite readily in concentrated solutions of alkalis with the formation of plumbites. Concentrated sulphuric acid also dissolves lead(II) sulphate, transforming it into the acid salt Pb(HSO₄)₂.

Lead(II) sulphide PbS is formed as a black precipitate when hydrogen sulphide reacts with lead(II) salts. This is why a paper wetted with a solution of a lead(II) salt rapidly darkens if the air contains

even insignificant amounts of hydrogen sulphide. This is used to detect H_2S .

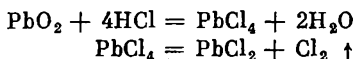
Reducing properties are not characteristic of lead(II) salts, unlike tin(II) salts. Compounds of lead(II) can be transformed into ones of lead(IV) only by means of very strong oxidizing agents.

Compounds of Lead(IV). *Lead dioxide* PbO_2 is a dark brown powder that forms when strong oxidizing agents react with the oxide or salts of lead(II). Lead dioxide, like tin dioxide, is an amphoteric oxide with acid properties predominating in it. Salts corresponding to plumbic acid H_2PbO_3 , which does not exist in the free state, are called **plumbates**. For example, the fusion of lead dioxide with calcium oxide yields calcium plumbate CaPbO_3 :



Most plumbates are insoluble in water. Sodium and potassium plumbates are soluble; they are greatly hydrolyzed in solution.

The basic properties of lead dioxide are exhibited in the formation of very unstable salts of lead(IV). For instance, when lead dioxide is reacted with hydrogen chloride, lead(IV) chloride PbCl_4 is formed at the first moment; however, it readily parts with chlorine and transforms into lead(II) chloride PbCl_2 :



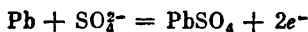
All lead(IV) compounds are very strong oxidizing agents. Lead dioxide PbO_2 finds practical application as an oxidizing agent in the chemical industry.

Two mixed oxides of lead are known: Pb_3O_4 and Pb_2O_3 . They can be considered as combinations of lead(II) and lead(IV) oxides, namely, $2\text{PbO} \cdot \text{PbO}_2$ (i.e. Pb_3O_4), and $\text{PbO} \cdot \text{PbO}_2$ (i.e. Pb_2O_3). **Red lead**, or **minium** Pb_3O_4 is a bright red substance. It is the basis of a paint used to protect metals from corrosion.

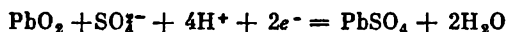
75. The Lead Accumulator

A lead (or lead-acid) accumulator ready for service consists of lead grids, one set of which is filled with lead dioxide and the other with metallic spongy lead. The grids are immersed in a 35-40% solution of H_2SO_4 ; at this concentration, the electrical conductivity of a sulphuric acid solution is maximum.

In operation of the accumulator—in its **discharge**—an oxidation-reduction reaction proceeds in it in the course of which the metallic lead is oxidized:



and the lead dioxide is reduced:



The electrons given up by the atoms of the metallic lead in oxidation are accepted by the lead atoms of the PbO_2 in reduction; the electrons are transferred from one electrode to the other through the external circuit.

Hence, the metallic lead is the anode in a lead accumulator and is charged negatively, while the PbO_2 is the cathode and is charged positively.

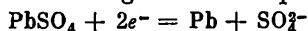
Migration of the ions occurs in the internal circuit (in the H_2SO_4 solution) when an accumulator is operating. The SO_4^{2-} ions migrate towards the anode, and the H^+ ions towards the cathode. The direction of this migration is due to the electric field appearing as a result of the electrode processes: anions are used up at the anode, and cations at the cathode. Hence, the solution remains electrically neutral.

If we add the equations corresponding to the oxidation of the lead and the reduction of the lead dioxide, we get the net equation of the reaction proceeding in a lead accumulator during its operation (discharge):

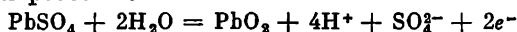


The e.m.f. of a charged lead accumulator is about 2 V. As an accumulator becomes discharged, the materials of its cathode (PbO_2) and anode (Pb) are used up. The sulphuric acid is also used up. The voltage across the accumulator terminals drops. When it becomes less than the value tolerated by the service conditions, the accumulator is charged again.

For **charging**, an accumulator is connected to an external source of direct current (its plus terminal is connected to the plus of the source, and the minus to the minus). The current flows through the accumulator in a direction opposite to that in discharging. As a result, the electrochemical processes at the electrodes are reversed. Now the following reduction process occurs on the lead electrode:

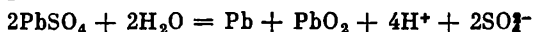


i.e., this electrode becomes the cathode. At the PbO_2 electrode, an oxidation process occurs:



consequently, this electrode is now the anode. The ions in the solution migrate in the directions opposite to those in which they travelled during operation of the accumulator.

Summating the last two equations, we get the equation of the reaction proceeding in the charging of an accumulator:



It is not difficult to notice that this process is opposite to the one occurring in operation of an accumulator: when an accumulator is charged, the substances needed for its operation are again produced in it.

6

COMMON PROPERTIES OF METALS. ALLOYS

In the preceding chapters, we treated the properties of non-metals and of only a few elements relating to metals. Before considering the remaining metals by groups of the periodic table, we shall stop to deal with their common properties and the ways of extracting them from their natural compounds.

76. Physical and Chemical Properties of Metals. The Electron Structure of Metals, Dielectrics, and Semiconductors

Metals have a number of common properties. The common physical properties of metals include their high electrical conductance, high thermal conductance, and **plasticity** or **ductility**, i.e. the ability to be deformed at ordinary and elevated temperatures without rupture. The ductility of metals is of a very great practical significance. Owing to this property, metals lend themselves to forging, rolling, drawing into a wire, and pressworking. Metals also possess a metallic lustre due to their good light reflecting power, and opacity (in a highly dispersed state, metals are usually black and dull).

Table 7 gives values of the electrical resistivity and thermal conductivity of selected metals. For comparison, the relevant data are also given for two non-metals—iodine and sulphur.

Table 7

Electrical Resistivity ρ and Thermal Conductivity λ
of Selected Elementary Substances at 20 °C

Substance	$\rho, \Omega \cdot \text{cm}$	$\lambda, J/(\text{cm} \cdot \text{s} \cdot \text{K})$	Substance	$\rho, \Omega \cdot \text{cm}$	$\lambda, J/(\text{cm} \cdot \text{s} \cdot \text{K})$
Aluminium	2.66×10^{-6}	2.26	Nickel	6.84×10^{-6}	0.586
Copper	1.61×10^{-6}	3.85	Silver	1.59×10^{-6}	4.586
Iron	9.71×10^{-6}	0.732	Iodine	About 10^{15}	—
Lead	20.6×10^{-6}	0.347	Sulphur	About 10^{23}	0.0025

In the chemical respect, all metals are characterized by a comparative readiness to give up their valence electrons and, as a consequence, by the ability of forming positively charged ions and exhibit only a positive oxidation state in their compounds. Many metals, for instance iron, chromium, and manganese, have different, but always positive, oxidation states in different compounds. In this connection, metals in the free state are reducing agents. The reducing power of different metals is not the same. For reactions in aqueous solutions, it is determined by the position of the metal in the electromotive series and the concentration (activity) of its ions in solution.

The reason for the common nature of both the physical and chemical properties of metals is the common nature of the structure of their atoms and of the crystal lattices of metals.

A common feature of metal atoms is their greater dimensions in comparison with non-metal atoms (see Vol. 1, Sec. 33). The outer electrons in metal atoms are at a considerable distance from the nucleus and are bound to it comparatively weakly—metal atoms are characterized by low ionization potentials (see Vol. 1, Sec. 34, Tables 4 and 5) and an affinity for an electron that is close to zero or negative. This is why metals readily part with their valence electrons, playing the role of reducing agents, and, as a rule, are not capable of gaining electrons, i.e. of exhibiting oxidizing properties.

Let us now consider the features of the structure of metals in the crystalline state. We have already noted that metals have a high electrical conductance, the current carriers in metals being electrons. This indicates that metals contain "free" electrons capable of moving along a crystal under the action of even weak electric fields. At the same time, non-metals in the crystalline state are usually dielectrics (insulators) and, consequently, contain no free electrons. These distinctions can be explained on the basis of the method of molecular orbitals (the MO method).

It was shown in Vol. 1, Sec. 45, that when two identical atoms interact, instead of the two initial atomic orbitals equivalent from the energy viewpoint, two molecular orbitals are formed that correspond to different energy levels (Vol. 1, Fig. 45). If three atoms interact, and their valence orbitals appreciably overlap, then not two, but three molecular orbitals are formed that belong to all three atoms to an equal extent (delocalized orbitals) and are characterized by three different energy values. With the consecutive increase in the number of interacting atoms, the addition of each of them leads to the formation of another energy level and to the further delocalization of the molecular orbitals (i.e. to their extension to a greater number of atoms); the total number of energy levels will equal the number of interacting atoms. Such a process is shown schematically in Fig. 31.

A glance at this figure shows that a growth in the number of atoms is attended by an increase in the number of allowed energy states and a decrease in the distance between adjacent energy levels. When the number of interacting atoms is small, a comparatively great energy has to be spent for transferring an electron from an energy level to the nearest higher one. But when the number of atoms N is great (in a macroscopic crystal N has the order of the Avogadro constant), adjacent levels differ so negligibly that a virtually continuous energy band is formed, and an electron can pass over to the nearest higher level with the expenditure of a negligibly small energy. If such a nearest level is not occupied by electrons, the electron at the preceding level behaves like a "free" one; owing to the delocalized nature of the orbitals it can travel along the crystal with infinitesimally small energy actions.

The molecular orbitals forming an energy band are filled in the order of the consecutive growth in the energy. In accordance with Pauli's principle, each MO can accommodate two electrons.

In a crystal of an alkaline metal, for example potassium, the atomic orbitals of the inner electron layers do not virtually overlap. It may be considered that in this case a continuous energy band is set up only at the expense of the outer electron layer orbitals and is filled by electrons of this layer. In a crystal containing N atoms, an energy band of N levels is formed from the initial atomic s orbitals of the outer layer. This band accommodates N outer s electrons of the alkali metal atoms, which occupy $N/2$ energy levels (two electrons at each level). The collection of these levels occupied by valence electrons is called a **valence band**. In the case being considered, the valence band occupies only half of the available energy levels. The other levels remain unfilled and form a **conduction band** (Fig. 32). Here, in direct proximity to the upper occupied levels, there are free levels which electrons can pass over to under the action of an electric field. This is exactly what makes it possible for electrons to carry a current, i.e. what ensures the electrical conductance of a metal.

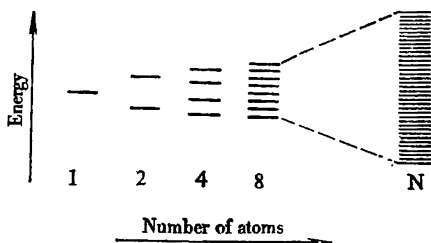


Fig. 31. Formation of energy levels when the number of interacting atoms grows

A band consisting of N levels is also formed in a crystal of a metal of the main subgroup of Group two (for example, calcium) from the initial atomic s orbitals of the outer layer. But, since here each atom has two outer s electrons, this band has to accommodate $2N$ electrons, so that all its levels will be completely occupied. Upon the interaction of the atoms of a metal, however, not only the outer s orbitals, but also the outer p orbitals overlap. The result is also the formation of a continuous energy band not filled by electrons. The bands formed by the s and p orbitals overlap (Fig. 33), so that in this case too the conduction band containing the free energy levels directly adjoins the valence band. Hence, the crystal considered must also have a high electrical conductance.

Figures 32 and 33 show a sharp boundary between the valence and conduction bands. Actually, this boundary is blurred; owing to thermal motion, electrons can pass from the upper levels of the valence band to the lower levels of the conduction band. The ability of these electrons to freely migrate along a crystal and carry energy from one part of it (heated) to another (colder) is the reason why metals have a high thermal conductance. Thus, both the electrical and the thermal conductance of metals are explained by the possibility of free migration of conduction band electrons. This is exactly why parallelism is observed between the values of the electrical conductance and thermal conductance for most metals. For instance, the best conductors of electricity—silver and copper—also have the highest thermal conductivity (see Table 7).

Heating is attended by more intensive oscillations of the atoms of a metal about their equilibrium positions in the crystal lattice, which hampers the motion of the electrons. Consequently, the electrical resistivity of metals grows with elevation of the temperature.

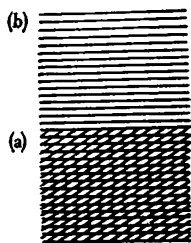


Fig. 32. Filling of energy levels by electrons in an alkali metal crystal:
 a—occupied levels (valence band);
 b—unoccupied levels (conduction band)

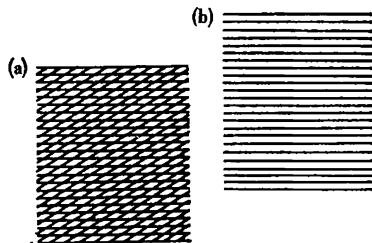


Fig. 33. Filling of energy levels by electrons in a crystal of a main subgroup metal of Group two:
 a—valence band formed from initial outer s orbitals;
 b—conduction band formed from initial outer p orbitals

The picture of the electron structure of solid metals considered above shows that the valence electrons establishing a chemical bond belong not to two or several definite atoms, but to the entire metal crystal. The valence electrons are capable of migrating within the crystal. The chemical bond thus formed is known as a **metallic bond**, and the collection of "free" electrons in a metal, as an **electron gas**. The metallic bond is characteristic of metals, their alloys, and inter-metallic compounds (see p. 220).

The ductility of metals is also explained by the specific properties of the metallic bond. When a solid body experiences a mechanical action, individual layers of its crystal lattice become displaced relative to one another. In crystals with an atomic structure, this results in breaking of the covalent bonds between the atoms belonging to different layers, and the crystal is demolished. In crystals with an ionic structure, mutual displacement of the layers inevitably leads to ions with a like charge being neighbours. Forces of electrostatic repulsion appear, and the crystal is also demolished. In a metal, however, displacement of individual layers of its crystal lattice is attended only by a certain redistribution of the electron gas bonding the metal atoms to one another, but the chemical bonds are not broken—the metal deforms without rupture.

Unlike metals, crystals of elementary substances formed by non-metals do not usually have an appreciable electronic conductance (see Table 7); they are dielectrics (insulators). Although continuous energy bands can also form here, the conduction band is separated from the valence one by a **forbidden band**, i.e. by a considerable energy gap ΔE (Fig. 34, dielectric). The energy of thermal motion or of a weak electric field is insufficient for surmounting this gap, and no electrons pass from the valence band to the conduction one. Thus, in dielectrics, the electrons cannot freely migrate along a crystal and be carriers of an electric current.

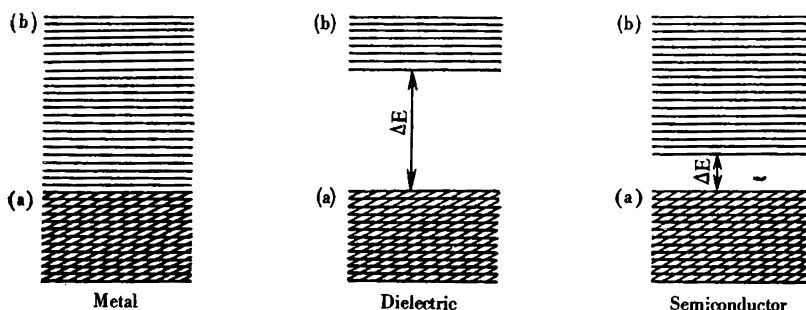


Fig. 34. Arrangement of energy bands in a metal, dielectric, and semiconductor: a—valence band; b—conduction band

Semiconductors have specific properties distinguishing them from both metals and dielectrics. At low temperatures, their electrical resistance is quite high, and in these conditions they display properties of dielectrics. But when heated or illuminated, the electrical conductance of semiconductors sharply grows and may reach values comparable with the conductance of metals.

The dependence of the electrical properties of semiconductors on the temperature and illumination is explained by the electron structure of their crystals. Here, as in dielectrics, the valence band is separated from the conduction band by the forbidden band (Fig. 34, semiconductor). But the width of the forbidden band ΔE is not great for semiconductors. Consequently, under the action of quanta of radiant energy or when heated, the electrons occupying the upper levels of the valence band can pass into the conduction band and carry an electric current. With elevation of the temperature or with a growth in the illumination, the number of electrons passing into the conduction band increases; accordingly, the electrical conductance of the semiconductor grows.

When electrons pass over to the conduction band, energy levels not completely occupied by electrons appear in the valence bands. They are known as electron vacancies or "holes". In an electric field, the holes behave like positive electric charges. Hence, a current can be carried in semiconductors both by the electrons of the conduction band (*n*-conductivity, from the word negative), and by the holes of the valence band (*p*-conductivity, from the word positive).

77. The Crystalline Structure of Metals

The structure of metals is studied in various ways. They can be divided into two groups. The first group includes methods of studying the internal structure of crystals, and the second—methods of studying their external forms.

The internal structure of crystals is studied chiefly with the aid of X-ray structural analysis (see Vol. 1, Sec. 50). Its data have been used to establish the kinds and parameters of lattices for all metals.

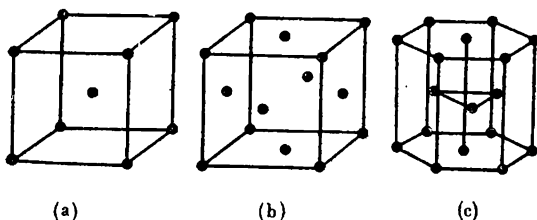


Fig. 35. Basic kinds of crystal lattices of metals:
a—body-centred cubic; *b*—face-centred cubic; *c*—hexagonal

The crystal lattices of metals may be of different kinds. Most metals, however, are characterized by three kinds of lattices: body-centred cubic (Li, Na, K, V, Cr, Fe*, Pb, W, etc.), face-centred cubic (Al, Ca, Fe**, Ni, Cu, Ag, Au, etc.), and hexagonal (Be, Mg, Cd, Ti, Co, Zn, etc.). Figure 35 shows the unit cells (see Vol. 1, Sec. 50) of these kinds of lattices.

The dimensions, shape, and mutual arrangement of the crystals in a metal are studied by **metallographic** methods. The most complete assessment of the structure of a metal in this respect is given by a microscopic analysis of its microsection. A sample is cut out from the metal being studied and its surface is ground, polished, and pickled in a special solution (a **pickling agent**). Pickling reveals the structure of the sample, which is examined or photographed with the aid of a **metallographic microscope**.

Metal crystals are usually small in size. Consequently, any metal article consists of a large number of crystals. This structure is called **polycrystalline**. When a metal crystallizes from the molten state, the growing crystals prevent one another from acquiring a regular shape. This is why the crystals of a polycrystalline body have an irregular shape and unlike regularly faced crystals are called **crystal-lites** or **grains**. The grains differ from one another in the spatial orientation of their crystal lattices (Fig. 36).

In the pickling of a microsection, the boundaries of the grains are eroded to a greater extent and become deeper. Light falling on them is scattered, and in the field of view of the microscope the boundaries of the grains seem dark, while the grains themselves are light (Fig. 37).

Special ways are used to obtain pieces of metals that are a single crystal—**monocrystals**. Monocrystals of metals, and also of non-metals, are prepared for scientific research and for special branches of engineering (semiconductors, lasers, etc.).

The internal structure of a metal grain is not strictly regular. Metals, like all real crystals (see Vol. 1, Sec. 51), have structural defects. Many properties of metals greatly depend on the nature and the number of the defects in the metal. For instance, vacancies play an important role in diffusion processes. These processes occur, for example, when the

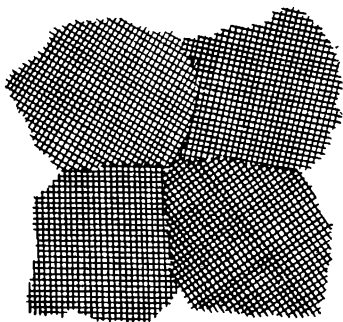


Fig. 36. Different orientations of crystal lattices in a polycrystalline body

* At temperatures up to 911 and from 1392 °C to melting.

** At temperatures from 911 to 1392 °C.

hot surface layer of a metal article is saturated with other elements for protection against corrosion or for imparting hardness to the surface of the article. The atoms of the foreign element penetrate into the metal chiefly at the sites of vacancies. The number of vacancies grows with elevation of the temperature, and this is one of the reasons why the diffusion process is accelerated.

Some mechanical properties of metals depend on the number of dislocations and their ability of migration along the metal. For instance, the high ductility of metals is explained by the migration of the dislocations.

Plastic shear in a metal crystal is shown schematically in Fig. 38. The external force F initially causes a slight displacement of the atoms in vertical rows 1, 2, and 3 (Fig. 38a). With an increase in the force F , this displacement grows, and row 1 of atoms (above shear plane AA) moves past the neutral position between $1'$ and $2'$. Row 2 transforms into a surplus plane and forms a dislocation (Fig. 38b), which we have already seen in Fig. 62 of Vol. 1 (p. 171). As a result of the formation of a dislocation, the lattice becomes distorted at both sides of the shear plane. Consequently, now even a small force F causes the vertical rows of atoms above the shear plane to become displaced—the dislocation like a relay race will be consecutively transferred to rows 3, 4, and so on.



Fig. 37. Microstructure of metal (magnification 100X)

At a certain moment, the position shown in Fig. 38c will occur. Finally, however, the dislocation will pass out onto the surface and will vanish as shown in Fig. 38d.

Thus, plastic shear in a real metal occurs not by simultaneous shear of an entire atomic plane, which would require the expenditure of much more energy, but by motion of the dislocations along the shear plane.

Metal crystals deprived of dislocations have a very high strength. Among them are the filamentary crystals or "whiskers" grown in special conditions. Their strength is many times superior to that of ordinary specimens of the relevant metal and is close to the theoretical value calculated for the crystal lattice of a metal having no structure defects.

On the other hand, the appearance of a very great number of differently oriented dislocations in a metal also leads to an increase in its strength because the crystalline structure of the metal is greatly distorted and migration of the dislocations is hampered. This explains the phenomenon of **work hardening**—hardening of a metal through plastic deformation. When a greatly deformed metal is heated, the distortions of its structure due to shear gradually vanish—the metal returns to a structurally more stable state; its ductility grows, while its hardness and strength diminish.

78. Extraction of Metals from Their Ores

The overwhelming majority of metals occur in nature in the form of compounds with other elements. Only a few metals are encountered in the free state. They are known as **native metals**. Gold and

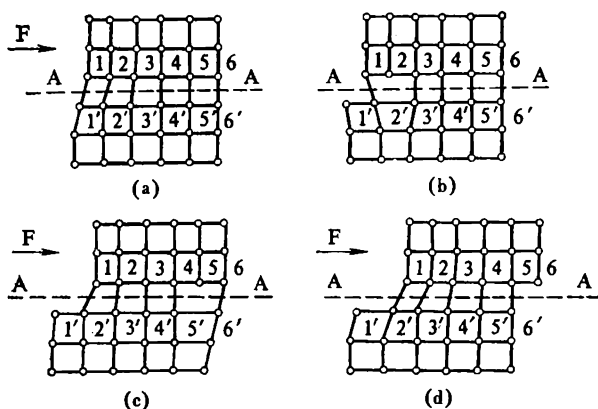


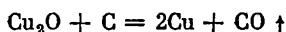
Fig. 38. Dislocation diagram of plastic shear

platinum occur almost exclusively in the native state, and silver and copper—partly. Native mercury and some other metals are also encountered.

Gold and platinum are extracted either by mechanical separation from the rock containing them, for example by washing, or by extraction from the rock with the aid of various reagents and the following separation from the solution. All other metals are extracted by the chemical processing of their natural compounds.

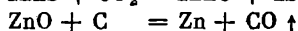
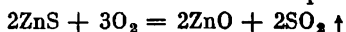
Minerals and rocks that contain metal compounds and are suitable for the industrial extraction of these metals are called **ores**. The main ores contain metal oxides, sulphides, and carbonates. The extraction of metals from their ores is the task of **metallurgy**—one of the most ancient branches of the chemical industry. Metallurgical processes occurring at high temperatures are known as **pyrometallurgical** ones. For example, iron and steel are produced in this way.

The most important method of extracting metals from their ores is based on reducing their oxides with coal or CO. If, for example, red copper ore Cu_2O is mixed with coal and heated, the coal reduces the copper and transforms into carbon monoxide, while the copper is recovered in the molten state:



Iron is smelted by reducing iron ores with carbon monoxide.

In processing sulphide ores, the sulphides are first converted to oxides by roasting in special kilns, and then the oxides obtained are reduced with coal. For example:



In addition to pyrometallurgical methods, **hydrometallurgical** ones are also used in extracting metals. They consist in the extraction of metals from their ores in the form of their compounds using aqueous solutions of various reagents with the following recovery of the metal from the solution. This method is used, for example, to recover gold (see Sec. 88).

Ores are usually a collection of minerals. Minerals containing the metal being extracted are called **ore minerals**, while all others are called **barren** or **dead rock**. The latter most frequently consists of sand, clay, and limestone, which are high-melting substances. To facilitate the melting of the metal, special substances called **fluxes** are mixed with the ore. The fluxes form low-melting compounds known as **slags** with the substances of the barren rock. The slags are usually gathered on the surface of the molten metal and are removed. If the barren rock is limestone, sand is used as the flux. For ores containing a large amount of sand, the flux is limestone. In both cases, calcium silicate is formed as the slag because sand mainly consists of silicon dioxide.

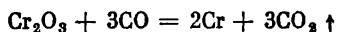
The content of barren rock in many ores is so great that the direct melting of the metal from such ores is not justified economically. The ores are preliminarily concentrated—part of the barren rock (gangue) is separated from them. The concentration of the ore mineral grows in the remaining concentrate. Ores are concentrated in various ways. The flotation, gravitational, and magnetic methods are in the greatest favour.

The **flotation** method is based on the different wettability of mineral surfaces by water. The finely comminuted ore is treated with water to which a small amount of a flotation reagent has been added that increases the difference between the wettabilities of the ore mineral and barren rock particles. Air is vigorously blown through the mixture formed; its bubbles adhere to the grains of the minerals that are wetted more poorly. These minerals are carried together with the air bubbles up to the surface and are thus separated from the barren rock.

Gravitational concentration is based on the difference in density and, consequently, in the speed of dropping of mineral grains in a liquid.

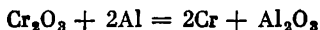
The **magnetic** method is based on the separation of minerals according to their magnetic properties.

Not all metals can be produced by the reduction of their oxides with coal or CO. Let us calculate, for instance, the standard Gibbs energy of the reaction of chromium reduction:



Using Table 7 of Vol. 1, p. 213, we find $\Delta G_{\text{form}}^\circ(\text{Cr}_2\text{O}_3) = -1059.0$ kJ/mol, $\Delta G_{\text{form}}^\circ(\text{CO}_2) = -394.4$ kJ/mol, and $\Delta G_{\text{form}}^\circ(\text{CO}) = -137.1$ kJ/mol, whence $\Delta G^\circ = 3(-394.4) - [-1059.0 + 3(-137.1)] = +267.1$ kJ. The value obtained is positive. This shows that at 25 °C and standard concentrations of the reactants, the reaction does not proceed in the desired direction. The positive value and great magnitude of ΔG° show that the reaction does not proceed in the direction of reduction of the metal not only in standard conditions, but also at temperatures and concentrations appreciably differing from the standard ones.

Stronger reducing agents such as hydrogen, magnesium, aluminium, and silicon are used for metals that cannot be reduced by carbon or carbon monoxide. The reduction of a metal from its oxide with the aid of another metal is known as **metallothermics**. If, particularly, aluminium is the reducing agent, then the process is called **aluminothermics**. Metals such as chromium and manganese are mainly produced by aluminothermics, and also by reduction with silicon. If we calculate ΔG° for the reaction



we get a negative value (-523 kJ). This indicates that chromium can be reduced by aluminium spontaneously.

Finally, metals whose oxides are the most stable (aluminium, magnesium, etc.) are produced by electrolysis (see Vol. 1, Sec. 103).

79. Production of Highly Pure Metals

The last few decades have seen a growth in the demand for highly pure metals in connection with the development of new branches of engineering. For example, the reliable operation of a nuclear reactor requires that the content in the fissioning materials of such "dangerous" impurities as boron and cadmium must never exceed millionths of a per cent. Pure zirconium—one of the best structural materials for atomic reactors—becomes absolutely unsuitable for this purpose if it contains even an insignificant admixture of hafnium. The germanium used as a semiconductor may contain not more than one atom of phosphorus, arsenic, or antimony per ten million atoms of the metal. Even a negligible admixture of lead or sulphur is absolutely prohibited in the heat-resistant alloys widely employed, for instance, in rocket building.

New methods of purifying substances have been developed for industrial purposes. We shall consider the most important of them.

Refining in a Vacuum. This method is based on the difference between the volatilities of the metal being purified and the impurities in it. The starting metal is charged into a special vessel connected to a vacuum pump. After evacuation of the vessel, its bottom part is heated. In the course of distillation, either the impurities* (if they are more volatile than the basic metal) or the purified metal (if the impurities are less volatile) are deposited on the cold parts of the vessel. Air must be continuously evacuated during the process because the presence of even small amounts of oxygen would result in oxidation of the surface of the molten metal and, consequently, in retardation of the evaporation process.

Zone melting consists in the slow pulling of a bar of the metal being purified through an annular furnace. The zone of the bar that is in the furnace at a given moment melts. As the bar is moved along, the molten zone travels from the beginning of the bar to its end.

Zone melting is used for a metal that has been preliminarily purified. The content of impurities in it is already not great, so that the basic metal and the impurities form a homogeneous solid solution. When the bar moves through the annular furnace, the metal melts at the front boundary of the zone and crystallizes at its rear boundary. The composition of the crystals formed that are in equilibrium with

* More exactly, in this case the basic metal greatly enriched with the impurities is deposited.

the melt differs from that of the melt (see p. 217). Impurities of one set of metals become concentrated in the molten zone and move together with it to the end of the bar; impurities of other metals are concentrated in the crystals formed, remain behind the moving zone and upon multifold repetition of the process move towards the beginning of the bar. As a result, the middle part of the bar is the purest; it is cut out and used.

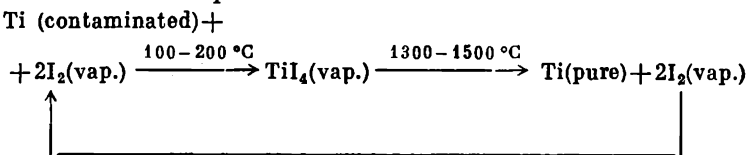
Zone melting is used to purify other substances in addition to metals.

Thermal Decomposition of Volatile Metal Compounds. *Carbonyl process.* This process is used to produce highly pure nickel and iron. Nickel to be purified is heated in an atmosphere of carbon monoxide under a pressure of about 20 MPa. The nickel reacts with the CO to form volatile nickel tetracarbonyl $\text{Ni}(\text{CO})_4$ (its boiling point is 42°C); the impurities contained in the starting metal do not participate in the reaction. The $\text{Ni}(\text{CO})_4$ formed is distilled off, and then heated to a higher temperature. As a result, the carbonyl decomposes with the separation of highly pure metal.

When iron is purified, synthesis and the following decomposition of iron pentacarbonyl $\text{Fe}(\text{CO})_5$ (boiling point 105°C) are conducted in a similar way.

The *iodide process* makes it possible to produce highly pure titanium, zirconium, and some other metals. Let us consider this process using titanium as an example. The initial metal in the form of a powder is heated to $100\text{--}200^\circ\text{C}$ with a small amount of iodine in a sealed apparatus. Titanium filaments heated by an electric current to $1300\text{--}1500^\circ\text{C}$ are stretched out in the apparatus. The titanium (but not the impurities) forms with the iodine the volatile TiI_4 that decomposes on the heated filaments. The pure titanium is deposited on them, while the iodine forms new portions of the iodide with the initial metal. The process goes on continuously until the entire metal is transferred to the titanium filaments.

The process can be represented as follows:



80. Alloys

The most diverse materials, both natural and man-made, are used to manufacture equipment in the various branches of today's industry. But the main part of modern equipment—machines and mechanisms—are manufactured chiefly from **metallic materials**—metals, alloys of metals with one another and with certain non-metals, first

of all with carbon. This is associated with the fact that of all kinds of materials, metal ones have the most valuable mechanical properties. In addition, the properties of metallic materials are very numerous and diverse.

In the liquid state, most metals dissolve in one another and form a homogeneous liquid alloy. Upon crystallization from the molten state, different metals behave in different ways. The following three cases are the main ones.

1. In the solid state, the metals being mixed do not dissolve and do not react chemically with one another. In these conditions, an alloy is a mechanical mixture and consists of crystallites of each of the two components* that can be clearly seen in a microsection (Fig. 39).

2. The metals being mixed react with each other to form a chemical compound.

3. In crystallization from a melt, the solubility of the metals in each other is retained. Homogeneous crystals are formed. In this case, the solid phase is called a **solid solution** (Fig. 40). For some metals, their mutual solubility in the solid state is unlimited, whereas other metals dissolve in each other only up to definite concentrations.

81. Phase Diagrams of Metal Systems

Of very great importance in studying the properties of alloys are **phase diagrams** characterizing the state of alloys of different compositions at different temperatures. Such diagrams show thermodynamically stable states, i.e. states corresponding to the minimum Gibbs energy of the system. They are also known as **equilibrium diagrams** because they show what phases can coexist in the given conditions.

Phase diagrams are obtained experimentally. This is usually done by plotting **cooling curves** and determining the temperatures of transformations according to the stops and points of inflection of the curves due to the heat effects of these transformations. To obtain the cooling curves, a number of mixtures of different compositions are prepared from the two metals of the system being studied. Each of these mixtures is melted. The liquid alloys (**melts**) obtained are slowly cooled, and the temperature of the cooling alloy is registered in definite intervals of time. The results of the observations are used to construct cooling curves by laying off the time along the axis of abscissas and the temperature along the axis of ordinates (Fig. 41).

The left part of Fig. 41 shows the form of a cooling curve for a pure

* There are apparently no metals that are absolutely insoluble in each other in the solid state. But when the mutual solubility of the metals does not exceed hundredths of a per cent, it is customary practice to consider that they are insoluble in each other.

molten metal. First, the temperature smoothly lowers along curve *ak*. At point *k*, the curve breaks, and the solid phase begins to form (crystallization), which is attended by the evolution of heat, owing to which the temperature remains constant for a certain time (the curve is parallel to the axis of abscissas). When all of the molten metal solidifies, the temperature again drops smoothly along curve *cb*.

Sometimes breaks in the dropping of the temperature are also observed on the cooling curve of a solid metal. This points to processes associated with the evolution of heat that occur in the solid substance, for example, a transition from one crystalline form to another.

The cooling curve for an alloy of two metals has a somewhat different form. Such a curve is shown at the right of Fig. 41. Point *k*, as on the first curve, corresponds to the beginning of solidification—the beginning of separation from the melt of crystals of one of the metals it contains. The composition of the melt that remains liquid changes, and the temperature of its solidification constantly lowers during

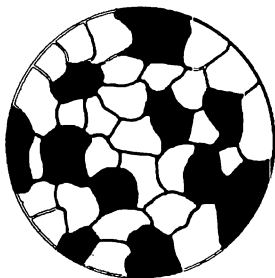


Fig. 39. Microstructure of a bimetal alloy forming a mechanical mixture

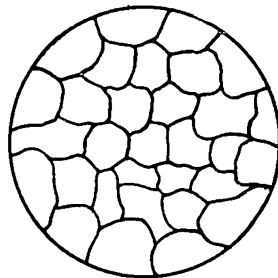


Fig. 40. Microstructure of a bimetal alloy forming a solid solution

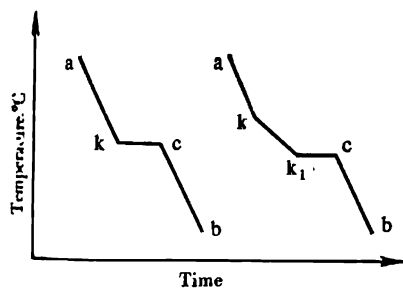


Fig. 41. Cooling curves

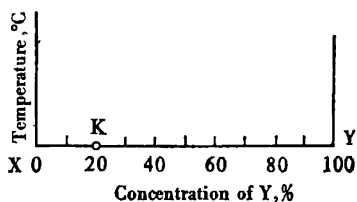


Fig. 42. Coordinates for plotting a phase diagram of a bimetallic system

crystallization. But the heat liberated in crystallization nevertheless retards the course of cooling, owing to which a break occurs in the curve at point *k*. Crystals separate, and the temperature smoothly lowers until a temperature is reached at which the alloy crystallizes without any change in its composition. Here the temperature stops dropping (point *k*₁). When crystallization terminates, the temperature drops along curve *cb*.

Having an adequate set of alloys with a varying content of the components and having determined in each alloy the temperatures of transformation, we can plot a phase diagram. In phase diagrams, the temperature is laid off along the vertical axis, and the composition of the alloy (the concentration of one of the components) along the horizontal one. For alloys consisting of two components designated by the symbols X and Y, their composition is characterized by a point on the section of the horizontal axis corresponding to 100%. The extreme points correspond to the individual components. Any point between the extreme ones characterizes the composition of a binary alloy. The numbers in Fig. 42 indicate the content of component Y. For instance, point K corresponds to an alloy consisting of 20% Y and 80% X.

Let us consider four simple cases—four kinds of diagrams corresponding to the kinds of alloys mentioned above: a mechanical mixture, a solid solution with unlimited solubility, one with limited solubility, and a chemical compound.

Phase Diagram for Alloys Forming Mechanical Mixtures of the Individual Components. Figure 43 shows a phase diagram of the system Pb-Sb as an example of phase diagrams of this kind. Points A and B in the diagram are the melting points of the system components: of lead (327 °C) and antimony (631 °C). In alloys of this kind, the addition of one component to another, according to Raoult's law, lowers the freezing (crystallization) point. Curve *AE* shows the temperature of crystallization of lead from melts rich in lead, and curve *BE* the temperature of crystallization of antimony from melts rich in antimony. Examination of the figure shows that an increase in the content of the second component lowers the freezing points of both the lead and the antimony. Point *E* belongs to both curves: both metals simultaneously crystallize from a melt whose composition corresponds to this point. This joint crystallization occurs at the lowest temperature. The composition cor-

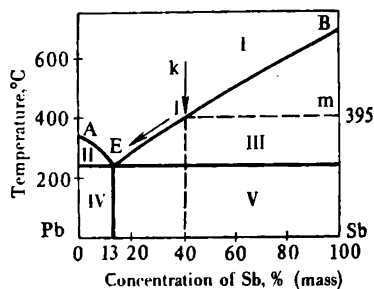


Fig. 43. Phase diagram of system Pb-Sb

responding to point *E* is called the eutectic composition, and the corresponding alloy is called a eutectic alloy or simply a eutectic (from the Greek "eutektos"—easily melted). For the system Pb-Sb, the eutectic consists of 13% Sb and 87% Pb; it melts and crystallizes at 246 °C.

Let us consider the crystallization of a melt in greater detail. Assume that we have a melt containing 40% Sb and 60% Pb (point *k* in Fig. 43). When this melt is cooled to 395 °C (point *l*), crystals begin to separate from it. They will be crystals of the component present in an excess amount in comparison with the eutectic, in the given case antimony. Now the melt consists of two phases. Two points correspond to it in the phase diagram: point *l* (melt) and point *m* (antimony crystals). The crystallization of a certain amount of antimony will change the composition of the melt; it will become leaner in antimony and, consequently, richer in lead. The point in the diagram corresponding to the melt will shift somewhat to the left. Since cooling is being continued, this point will again reach the curve—a certain amount of antimony crystals will again separate from the melt. Hence, as cooling and crystallization continue, the point corresponding to the melt moves downward and to the left along the antimony crystallization curve, while the point corresponding to antimony crystals moves downward along the right-hand vertical axis. When the melt reaches the eutectic composition, very fine crystals of both components (the eutectic) will begin to separate from it, until the entire amount of the substance taken crystallizes. The alloy obtained will be a mixture of the eutectic with antimony crystals.

If we start with a melt containing a small percentage of antimony (less than the eutectic amount), the entire process will occur similar to that described above, the only difference being that first crystals of lead will separate instead of antimony. The alloy obtained will have a structure that is a mixture of the eutectic with lead crystals. Finally, if we start with a melt having the eutectic composition, the entire melt will crystallize at 246 °C and will be a eutectic. Figure 44 shows the structure of alloys of the system Pb-Sb.

If the upper curves in the diagram in Fig. 43 (*AE* and *BE*) show the temperature of the beginning of crystallization, then the lower one—the horizontal line passing through point *E*—shows the temperature at which crystallization of the melt terminates. A glance at the figure shows that for systems having phase diagrams of the kind being considered, the temperature of termination of crystallization does not depend on the composition of the mixture.

In the melting of solid alloys, the horizontal line passing through point *E* shows the temperature of the beginning of melting. In the case being considered, this temperature does not depend on the composition of the melt because melting begins from the eutectic

contained in all alloys of the system (except for the individual components). The temperature of the alloy will remain constant until all the eutectic contained in it melts. Further heating results in elevation of the temperature—the crystals of the pure component that in the initial alloy were mixed with the eutectic begin to melt. The composition of the melt will become richer in this component, and the point corresponding to the melt will move along the relevant

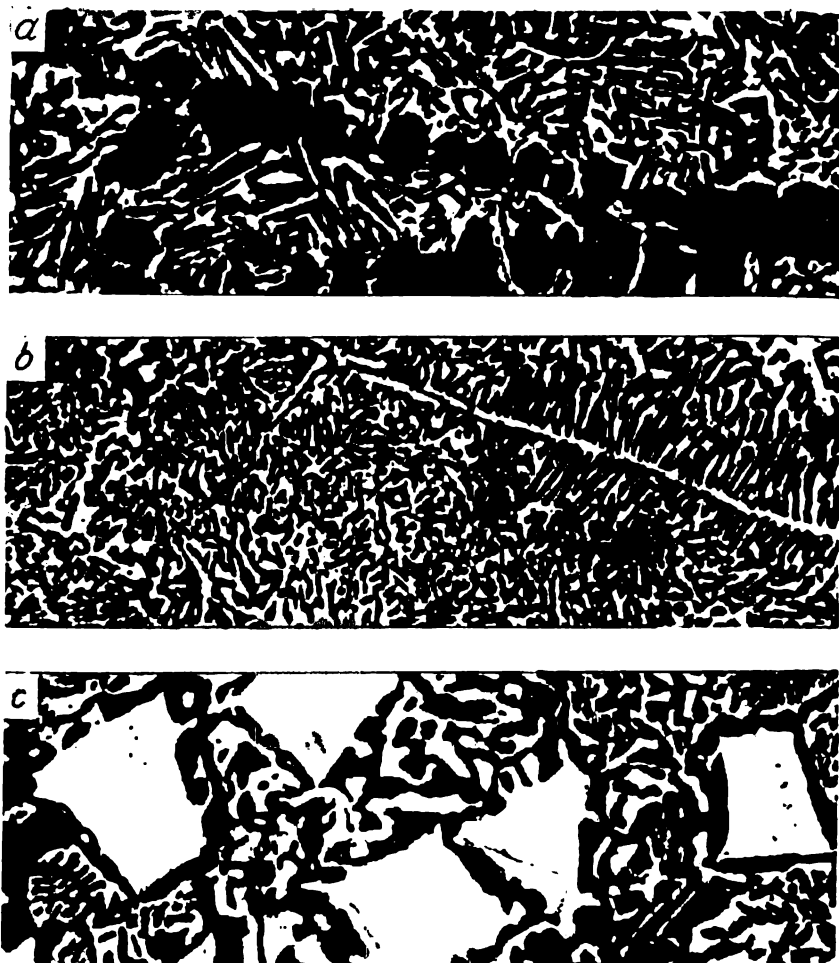


Fig. 44. Structure of lead-antimony alloys:

a—alloy containing excess of lead; *b*—eutectic alloy; *c*—alloy containing excess of antimony

branch of the upper curve. When melting terminates, i.e. when the solid phase vanishes, the composition of the melt will be the same as that of the initial alloy. Thus, if we start with a solid alloy, the horizontal line passing through point *E* shows the temperature of the beginning of melting, while curves *AE* and *BE* show the termination of melting.

It is clear from what has been said above that region *I* in the diagram in Fig. 43 depicts a melt, regions *II* and *III* depict the coexistence of a melt and crystals of the excess component, and regions *IV* and *V* depict a mixture of the eutectic with grains of lead (region *IV*) or antimony (region *V*).

We have already mentioned that the composition of the alloy taken is laid off along the horizontal axis of the diagram. But for regions corresponding to the equilibrium of two phases, we can use this axis to find the compositions of these phases. Assume, for instance, that an alloy of 5% Sb and 95% Pb is heated to 270 °C. Point *a* in the phase diagram (Fig. 45) corresponds to this alloy. We draw through this point a horizontal line up to its intersection with the nearest lines of the diagram. This gives us points *b* and *c*. They show that equilibrium of lead crystals (point *b*) with a melt whose composition is determined by the abscissa of point *c* (approximately 10% Sb and 90% Pb) corresponds to the alloy taken at 270 °C.

Phase Diagram for Alloys with Unlimited Solubility in the Solid State. Figure 46 contains a phase diagram of the system Ag-Au that is a very simple example of this kind of diagrams. As in the preceding cases, points *A* and *B* represent the melting points of the components. The shape of the melting (bottom) and freezing (top) curves is due in this case to the fact that the crystals separating when the melt is cooled always contain both components (except, naturally, in the crystallization of pure silver or gold).

Let us see how the melts crystallize in this case. Assume that the initial liquid alloy corresponds to point *d* in the diagram (Fig. 46).

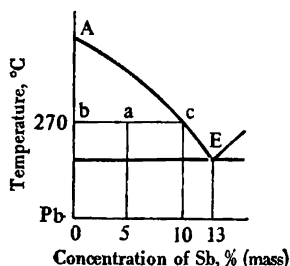


Fig. 45. Part of phase diagram of system Pb-Sb

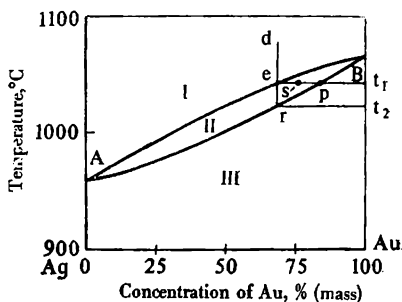


Fig. 46. Phase diagram of system Ag-Au

When it is cooled to the temperature t_1 (point e), crystallization begins. The crystals are a solid solution richer in the refractory component—gold (point p). Consequently, in the course of crystallization, the liquid phase becomes leaner in the refractory component, and the point in the diagram corresponding to the melt shifts somewhat to the left. As cooling proceeds, this point moves downward, again reaches the curve, and crystallization continues. Thus, cooling of the melt is attended by separation of crystals of a solid solution enriched in the refractory component—gold, and enrichment of the melt in the low-melting component—silver. The corresponding points in the diagram shift: the composition of the liquid phase changes along the top line, and that of the solid solution along the bottom one. When the process is conducted slowly, crystallization terminates when a temperature t_2 is reached at which the crystals formed have the composition of the initial alloy (point r).

Thus, region *I* in the phase diagram of the system being considered (Fig. 46) depicts a melt, region *II*—the coexistence of a melt and crystals of the solid solution, and region *III* depicts a solid solution. In equilibrium, the points on both curves in the diagram are related: for each temperature there are a melt of a definite composition and crystals also of a definite composition, but different than that of the melt (for example, point p corresponds to point e).

In the course of crystallization, the temperature of the system lowers, and equilibrium between the melt and the crystals formed earlier, i.e. at a higher temperature, is violated. Therefore, crystallization is attended by diffusion as a result of which, in slow conduct-

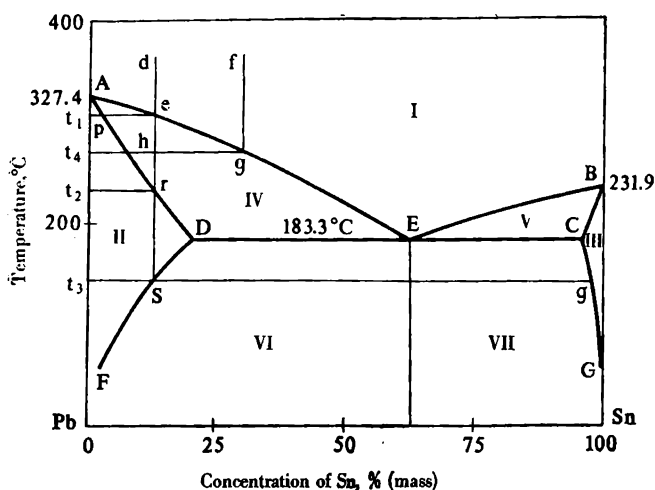


Fig. 47. Phase diagram of system Pb-Sn

ing of the process, the grains of the entire alloy are homogeneous and have the same composition. In rapid cooling, the diffusion processes do not have time to occur, and the alloy is not homogeneous.

As in the preceding case, the compositions of the equilibrium phases—the melt and the solid solution in equilibrium with it—can be established along the horizontal axis of the diagram. For instance, the system which point *s* corresponds to consists of a melt whose composition corresponds to point *e*, and crystals of a composition corresponding to point *p*.

Phase Diagram for Alloys with Limited Mutual Solubility in the Solid State. In alloys of this kind formed by the components *X* and *Y*, a liquid phase and two solid solutions can exist: a solution of component *X* in *Y* and a solution of component *Y* in *X*. In the simplest case, these two solid solutions form a eutectic. The system Pb-Sn whose phase diagram is shown in Fig. 47 belongs to this kind. We shall note first of all that here region *I* depicts a melt, region *II* a solid solution of tin in lead, and region *III* a solid solution of lead in tin.

To understand what phases the other regions in the diagram and the curves on it correspond to, let us consider how melts crystallize in a system of this kind.

We shall first proceed from a liquid alloy rich in lead (point *d* in Fig. 47). When this melt is cooled to the temperature t_1 (point *e*), separation of crystals of a solid solution of tin in lead will begin. The composition of these crystals corresponds to point *p*; they are richer in lead than the initial melt so that in crystallization, the melt becomes leaner in lead. As in the preceding cases, the points in the diagram corresponding to the melt and the crystals formed shift: the composition of the liquid phase changes along line *AE*, and that of the crystals along line *AD*. When the temperature t_2 is reached (point *r*), the crystals formed have the composition of the initial alloy. If the process is conducted sufficiently slowly, then at the temperature t_2 crystallization terminates as in systems with unlimited mutual solubility (see above).

Curve *ADF* shows the solubility of tin in solid lead at different temperatures. The solubility can be seen to be the greatest at 183.3 °C. Consequently, when the crystals cool to the temperature t_3 (point *s*), the solid solution becomes saturated. A transformation in the solid state begins in it: crystals of the solid solution based on lead whose composition corresponds to point *s* will transform into crystals of the solid solution based on tin whose composition corresponds to point *q*. At a constant temperature, the crystals of these two solid solutions will be in equilibrium. Upon further cooling, however, equilibrium will be violated, and the transformation of one set of crystals into another will continue. The crystals of the lead-based solid solution will become lean in tin—their composition will

vary along curve DF , simultaneously the composition of the tin-based crystals of the solid solution will change along curve CG .

Now let us consider the cooling of a liquid alloy that is not so rich in lead (point f). Upon cooling to the temperature t_4 (point g), crystals of the lead-based solid solution will begin to separate from the melt; their composition corresponds to point h . As these crystals separate, the melt becomes richer in tin: its composition changes along line AE , and that of the separating crystals along line AD . When the point corresponding to the melt reaches point E , crystals of both solid solutions separate from the melt, the composition of the crystals of the lead-based solid solution corresponds to point D , and that of the crystals of the tin-based solid solution to point C . It is obvious that point E is the eutectic point, and the separating mixture of crystals is the eutectic mixture.

In the region of temperatures below 183.3°C , the solubility of lead in tin and of tin in lead diminishes with lowering of the temperature. Hence, upon further cooling of the alloy, the composition of the crystals formed changes. That of the crystals of the solid solution of tin in lead changes along curve DF , and of the crystals of the solid solution of lead in tin along curve CG .

The crystallization of melts rich in tin occurs in a similar way. In this case, crystallization begins with liberation of the tin-based crystals of the solid solution.

We can conclude from the above that regions IV and V in the diagram depict the coexistence of a liquid melt and crystals of the lead-based (region IV) or tin-based (region V) solid solution, while regions VI and VII depict mixtures of the eutectic crystals with crystals of the lead-based and tin-based solid solution, respectively.

Phase Diagram for Alloys Forming Chemical Compounds. Metals form numerous intermetallic compounds. The enthalpies of formation of such compounds are generally small, only in separate cases (for instance, when aluminium reacts with molten copper) is their formation attended by a considerable exothermic effect. Many metals form several compounds, for example AuZn , Au_3Zn_5 , AuZn_8 , Na_4Sn , NaSn , NaSn_2 .

Figure 48 shows a phase diagram of the system Mg-Pb . This is a very simple example of systems in which chemical compounds are formed: lead forms only one compound Mg_2Pb with magnesium, while in the solid state these metals do not dissolve in each other.

This diagram differs from those considered earlier in the presence of a maximum on the curve of the beginning of crystallization. This maximum (point C) corresponds to the melting point of the compound Mg_2Pb . The abscissa of the maximum point indicates the composition of the compound. The diagram contains two eutectics E_1 and E_2 . Eutectic E_1 is a mixture of Mg and Mg_2Pb crystals, while eutectic E_2 is a mixture of Pb and Mg_2Pb crystals.

Thus, a diagram of a system with a chemical compound consists, as it were, of two diagrams of the first kind. If the components of the system form two or more chemical compounds with one another, then the diagram consists, as it were, of three, four, and more separate diagrams of the first kind.

The crystallization of alloys in this and similar cases occurs similarly to the crystallization of alloys forming diagrams of the first kind. The difference is that crystals of the compound are formed in addition to the separation of crystals of the individual components. In cooling, magnesium separates from melts along line AE_1 , lead along line E_2B , and Mg_2Pb along line E_1CE_2 . For instance, if we cool a liquid alloy containing 40% Pb (i.e., 60% Mg), then magnesium crystals will first separate from it. When the temperature lowers to 460 °C, the entire remaining liquid part of the alloy will begin to solidify at this temperature, forming a eutectic mixture of very fine crystals of magnesium and the chemical compound Mg_2Pb .

When a liquid alloy containing 75% Pb is cooled, first Mg_2Pb crystals will separate. This will occur until the temperature lowers to 460 °C—the eutectic temperature. Similar processes with the separation of the eutectic E_2 (at 250 °C) will occur when the alloy contains more than 80% Pb.

It is not difficult to see that region *I* in Fig. 48 depicts the liquid alloy, regions *II* to *V* depict equilibria of the liquid alloy and the relevant crystals (in region *II*—Mg crystals, in regions *III* and *IV*— Mg_2Pb crystals, in region *V*—Pb crystals), and regions *VI*–*IX* depict solid alloys [Mg + eutectic E_1 (*VI*), Mg_2Pb + eutectic E_1 (*VII*), Mg_2Pb + eutectic E_2 (*VIII*), and Pb + eutectic E_2 (*IX*)].

We have considered the simplest, but at the same time the most important kinds of phase diagrams. For many systems, the phase

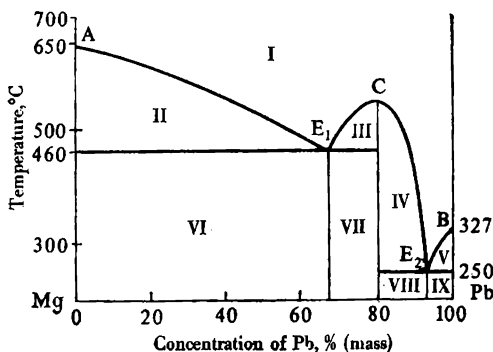


Fig. 48. Phase diagram of system Mg-Pb

diagrams have a considerably more complicated nature. For example, a number of metals and alloys undergo transformations in the solid state, passing from one modification to another. The relevant phase diagrams contain curves dividing the regions of stability of these modifications.

There are methods for constructing the phase diagrams of ternary systems, i.e. systems consisting of three components.

The phase diagrams for technically important systems have been studied and are given in special publications. They find a widespread application in various fields of science and engineering, are a scientific foundation for the choice of alloys having given properties, in investigating methods of the thermal processing of alloys, and in developing and creating new alloys. An example of a system having a very great practical importance is the Fe-C system. The phase diagram of this system is treated in Sec. 124.

In addition to phase diagrams, of great significance are composition-property diagrams. In these diagrams, the composition of the system is laid off along the axis of abscissas, as in phase diagrams, while quantities characterizing various properties of the system, for instance the density, electrical conductance, and resistance to corrosion, are laid off along the axis of ordinates.

The top of Fig. 49 schematically shows phase diagrams for the four main kinds of alloys, while its bottom shows the typical "composition-property" diagrams corresponding to them. It can be seen

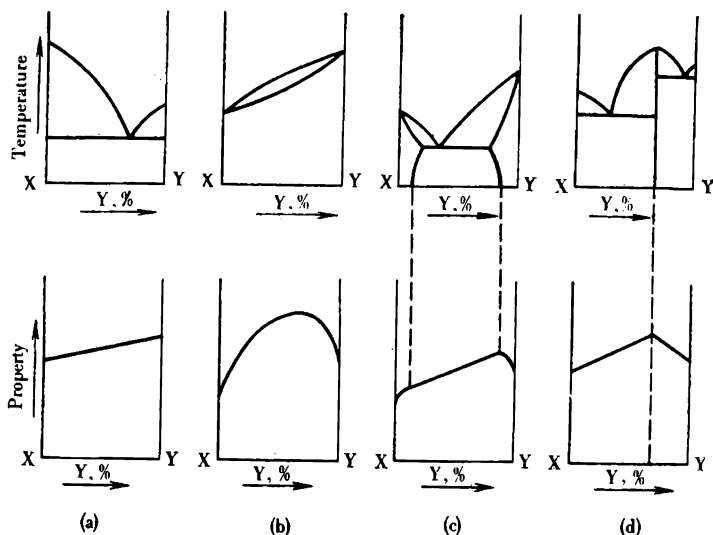


Fig. 49. Typical phase diagrams and the shape of the "composition-property" diagrams corresponding to them

that in the formation of a mechanical mixture (Fig. 49a), the properties of alloys change linearly and their values are within the interval between the values of these properties for the individual components. A non-linear relation is observed for the formation of solid solutions (Fig. 49b and c). Some properties here may differ quite considerably from those of the metals forming the alloy. Finally, when a chemical compound is formed, a maximum or minimum corresponding to the compound appears in the "composition-property" diagrams.

N. Kurnakov* used the method of constructing "composition-property" diagrams as the basis of the method of physicochemical analysis which he developed for investigating systems. At present, physicochemical analysis is one of the main ways of studying alloys and in general systems consisting of several components: salts, oxides, etc.

82. Corrosion of Metals

Metallic materials—metals and alloys based on metals, when coming into contact with their environment (gaseous or liquid) are subjected to destruction at a certain rate. The cause of this destruction is chemical reaction: metals enter into oxidation-reduction reactions with substances surrounding them and become oxidized.

The spontaneous destruction of metallic materials occurring as a result of the chemical action of their environment is known as corrosion.

The total mass of the metallic materials used in the form of various articles in the world's economy is very great. Consequently, notwithstanding the generally low rate of corrosion, enormous amounts of metal are lost irretrievably every year owing to corrosion. Approximate calculations show that the world's loss of metal due to corrosion amounts to 20 million tonnes a year. But still greater harm is associated not with the loss of metal, but with spoiling of articles caused by corrosion. The outlay for the repair or replacement of components of vessels, motor vehicles, chemical apparatus, and instruments is many times greater than the cost of the metal which they are made from. Finally, the indirect losses caused by corrosion are also appreciable. Among them are, for example, the leakage of oil or gas from corroded pipes, the spoiling of food products,

* Nikolai Semenovich Kurnakov (1860-1941), a Russian scientist, academician, State Prize winner, is the author of works on the theory of solutions and alloys, the chemistry of complex compounds, and is the founder of physicochemical analysis. He gave much attention to studying the nature of salt solutions; his works in this field facilitated the effective use of the country's salt resources and led to the discovery of potassium salt deposits near Solikamsk.

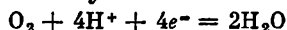
and the loss of health and sometimes even the life of people when this is due to corrosion. Hence, the combatting of corrosion is an important problem of the national economy. This is why huge sums are spent for protection against corrosion.

The most important cases of corrosion include corrosion in gases (gas corrosion) and corrosion in solutions of electrolytes (electrochemical corrosion). Corrosion in gases occurs at elevated temperatures when the condensation of moisture on the surface of a metal is impossible. The fittings of furnaces, the components of internal combustion engines, the blades of gas turbines, etc. are corroded by gases. Metal subjected to heat treatment also undergoes gas corrosion. Gas corrosion results in the formation of the relevant compounds—oxides, sulphides, etc.—on the surface of a metal.

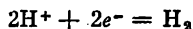
Heat-resistant alloys are used to manufacture apparatus coming into contact with corroding gases. Iron and steel are made heat-resistant by adding chromium, silicon, and aluminium to them, alloys based on nickel or cobalt are also used. Protection against gas corrosion is also provided by saturating the surface of an article in the hot state with certain metals having a protective action. These metals are aluminium and chromium. Their protective action is due to the formation on their surface of a very thin but strong oxide film preventing reaction of the metal with its environment. When aluminium is used, this method is called **aluminizing**, and when chromium is used—**thermochromizing**.

Electrochemical corrosion includes all cases of corrosion in aqueous solutions. For example, the underwater parts of vessels, steam boilers, and pipelines laid in the earth are subjected to electrochemical corrosion. The corrosion of metal in a humid atmosphere is also electrochemical corrosion. As a result of electrochemical corrosion, the oxidation of a metal may lead either to the formation of insoluble products (for instance, rust), or to the transition of the metal into solution in the form of ions.

Water usually contains dissolved oxygen capable of being reduced:

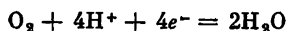


In addition, water contains hydrogen ions also capable of being reduced:



Dissolved oxygen and hydrogen ions are the most important oxidizing agents that cause the electrochemical corrosion of metals.

Let us see what metals can be oxidized by the oxygen dissolved in water and what by the hydrogen ions. The potential corresponding to the electrode process



is (see Table 18 in Vol. 1, p. 300):

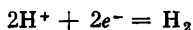
$$\varphi = 1.228 - 0.059 \text{ pH}$$

In neutral media ($\text{pH} = 7$), it will have the value:

$$\varphi = 1.228 - 0.059 \times 7 \approx 0.8 \text{ V}$$

Consequently, the oxygen dissolved in water or in a neutral aqueous solution can oxidize the metals whose potential is lower than 0.8 V; they occupy the part of the electromotive series from its top to silver.

The potential corresponding to the electrode process



in a neutral medium is about -0.41 V (see Vol. 1, p. 304). Hence, the hydrogen ions in water and in neutral aqueous solutions can oxidize only the metals whose potential is less than -0.41 V —these include the metals from the top of the electromotive series to cadmium. It must be noted that cadmium and the metals close to it in the electromotive series have on their surface a protective oxide film preventing their reaction with water. Therefore, the number of metals that can be oxidized by the hydrogen ions in neutral media is still smaller.

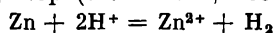
Thus, water containing dissolved oxygen is much more dangerous as a corroding medium than water that does not contain it and can oxidize metals only with hydrogen ions.

When metallic materials are used, the question of the rate of their corrosion is very important. In addition to the nature of the metal and the oxidizing agent and to the concentration of the latter, the rate of corrosion can be affected by various impurities contained both in the metal itself and in the corroding medium—in the atmosphere or the solution.

Two different cases can be observed in the corrosion of a metal containing inclusions of another metal, depending on the amount of the inclusions.

The Amount of the Inclusions of the Foreign Metal Is Very Small. These inclusions do not virtually change the magnitude of the potential of the basic metal in the given solution. In this case, acceleration of corrosion may be observed if the overvoltage of the oxidizing half-reaction on the inclusion metal is less than on the basic metal.

We can indicate as an example the corrosion of zinc containing small admixtures of iron or copper in hydrochloric or dilute sulphuric acid. When the zinc contains only hundredths of a per cent of any of these metals, the rate of its reaction with the above acids is hundreds of times higher than for zinc that has been subjected to special purification. The explanation is that the overvoltage of the liberation of hydrogen on copper and on iron is lower than on zinc, while the limiting step (see Vol. 1, Sec. 61) of the reaction



is exactly the process of reduction of the hydrogen ions.

The Amount of the Inclusions of the Foreign Metal Is Considerable. The potential of such inclusions differs from that of the basic metal. In this case, in addition to the magnitude of the overvoltage of the oxidizing half-reaction on the inclusion metal, the rate of corrosion may be affected by the polarizing action (see Vol. 1, Sec. 104) of the inclusion metal on the basic one. If the inclusion metal has a higher potential than the basic one, the latter is subjected to anode polarization, and the rate of its corrosion grows. For example, aluminium containing inclusions of iron or copper corrodes much more rapidly than highly pure aluminium.

The rate of corrosion of a metal also grows when it contains non-metallic impurities whose potential is higher than that of the basic metal. For instance, inclusions of oxides or slags in steel greatly lower its resistance to corrosion.

The impurities contained in the environment may be absorbed on the surface of a metal and also catalytically affect corrosion, accelerating or inhibiting it. For example, most iron alloys corrode much more rapidly in sea water than in water having the same oxygen concentration, but containing no chlorides. This is due to the fact that the chloride ions adsorbed on the surface of the iron prevent the formation of protective layers on it.

We mentioned in Vol. 1 (p. 304) that some metals in definite conditions become passive—layers or films consisting of adsorbed oxygen, of an oxide of the given metal, or its salt are formed on its surface. The presence of such layers and their structure greatly affect the rate of corrosion of a metal. In a number of cases, these layers have a protective action owing to which the metal corrodes only at a negligibly slow rate. In the atmospheric air, passivating films are formed on chromium, nickel, aluminium, and zinc.

Important cases of electrochemical corrosion include corrosion in natural water, in solutions, atmospheric corrosion, corrosion in the soil, corrosion in non-uniform aeration, and contact corrosion.

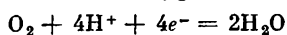
Atmospheric corrosion is corrosion in humid air at room temperature. The surface of a metal in humid air may be coated with a film of water containing various gases, first of all oxygen. The rate of atmospheric corrosion depends on the conditions. Particularly, it is affected by the humidity of the air and the content in it of gases forming acids with water (CO_2 , SO_2). The state of the metal's surface is also of great significance: the rate of atmospheric corrosion grows sharply when a surface has roughnesses, microcracks, pores, gaps, and other spots facilitating the condensation of moisture.

Corrosion in soil* leads to the destruction of underground pipes, cable sheathings, and components of structures. The metal in these cases comes into contact with the moisture of the soil containing

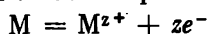
* This kind of corrosion is often inaccurately called soil corrosion.

dissolved air. Depending on the composition of the ground water, and also on the structure and mineralogical composition of the soil, the rate of this kind of corrosion may be very diverse.

Corrosion in non-uniform aeration is observed when a component or a structural member is in a solution, but the access of dissolved oxygen to its different parts is not the same. The parts of the metal to which the access of oxygen is minimum corrode to a much greater extent than the parts to which the access of oxygen is greater. Such a non-uniform distribution of corrosion is explained as follows. In the reduction of oxygen



hydrogen ions are consumed, and the solution, consequently, becomes somewhat more alkaline. Metals, and particularly iron, become passive more readily in an alkaline solution. Therefore, the aerated parts of the metal become passive, and the rate of corrosion on them diminishes. On non-aerated parts, no passivation occurs—here a metal oxidation process occurs, and its ions pass into solution:



Hence, in non-uniform aeration of a metal, spatial separation of the oxidation-reduction reaction occurs: oxygen is reduced on the more aerated sections, and the metal is oxidized on the less aerated sections of the surface. Localization of the oxidation process results in **local corrosion**—the intensive destruction of the metal on separate sections. Local corrosion leads to the appearance of pits on the surface of the metal that with time may transform into through holes. It is sometimes difficult to detect the development of pits, for example owing to the remnants of scale on the surface of the metal. This kind of corrosion is especially dangerous for the sheathing of vessels, for industrial chemical equipment, and in a number of other cases.

Contact corrosion may occur when two metals with different potentials come into contact with each other either in an aqueous medium or in the presence of moisture condensing from the air. As in the case of considerable inclusions treated above, the metals have a polarizing action on each other: the metal with the lower potential is subjected to anode polarization, and the rate of its corrosion near the place of contact sharply grows.

Contact corrosion is observed, for example, in heat supply plants when the copper heating coils are joined to iron boilers or pipes. Intensive corrosion of the iron occurs near the joints. But the ratio between the potentials of the contacting metals depends not only on the nature of the metals, but also on that of the substances dissolved in the water, on the temperature, and on other conditions, and does not always correspond to the mutual position of the metals in the electromotive series. For instance, when iron and zinc come into

contact, the latter intensively corrodes at room temperature, but in hot water the polarity of the metals changes, and the iron begins to dissolve.

A variety of methods are used to prevent electrochemical corrosion and afford protection from it. The most important of them are as follows:

- (1) the use of chemically stable alloys;
- (2) the protection of the metal surface with coatings;
- (3) treatment of the corrosive medium;
- (4) electrochemical methods.

Among chemically stable alloys, the greatest favour is given to stainless steels, whose composition includes up to 18% chromium and up to 10% nickel.

The coatings used for the protection of metals can be metal, non-metal, and those formed as a result of chemical or electrochemical processing of the metal surface.

The metals forming protective films on their surface are generally used as coating ones. We have already mentioned that these metals include chromium, nickel, zinc, cadmium, aluminium, tin, and some others. Metals having a high electrode potential—silver and gold—are used much less frequently. There are various ways of applying metal coatings; the methods of electroplating (see Vol. 1. Sec. 103) have the greatest advantages.

Non-metallic coatings include lacquers, varnishes, paints, enamels, phenol formaldehyde, and other resins. The greatest preference is given to various surface finishes for prolonged protection of metal structures, components, machines, and instruments against corrosion.

The coatings produced by the chemical or electrochemical treatment of a metal are mainly protective oxide or salt films. Examples are the oxidizing of aluminium (the creation on its surface of stable oxide films), and the phosphorizing of steel articles (the creation of protective films consisting of phosphates).

The method of treating the environment is suitable for cases when the article to be protected is used in a restricted volume of liquid. The method consists in removing dissolved oxygen from the solution in which the component being protected is used (**de-aeration**) or in adding substances retarding corrosion—**inhibitors**—to the solution. Various inhibitors are used depending on the nature of the metal and the solution: sodium nitrite, potassium chromate and dichromate, sodium phosphates, certain high-molecular organic compounds, and others. The protective action of these substances is due to the fact that their molecules or ions are adsorbed on the surface of the metal and catalytically diminish the rate of corrosion, while some of them (for instance, chromates and dichromates) transfer the metal into the passive state.

The electrochemical methods of metal protection include cathode protection and the method of protectors. In **cathode protection**, the structural member or component being protected is connected to the negative pole of a source of electrical energy and becomes the cathode. Pieces of iron are used as the anodes. When the current is appropriate in the circuit, the oxidizing agent is reduced on the article being protected, while the substance of the anode is oxidized.

The **method of protectors** is carried out by attaching a large plate made from a more active metal—a protector—to the metal being protected. The protector of steel articles is usually made of zinc or a magnesium-based alloy. With a good contact between the metals, the metal being protected (iron) and that of the protector (for instance zinc) have a polarizing action on each other. According to the mutual position of these metals in the electromotive series, the iron undergoes cathode polarization, and the zinc—anode polarization. As a result, the reduction of the oxidizing agent present in water (generally dissolved oxygen) occurs on the iron, while the zinc is oxidized.

Both protectors and cathode protection can be employed in media that are good conductors of an electric current, for instance in sea water. Particularly, protectors are widely used for protecting the underwater parts of seagoing vessels. It is quite obvious that the losses incurred as a result of corrosion of the hull of a seagoing vessel and the associated loss of time for repairs are very great and exceed the cost of the protectors many times.

7

FIRST GROUP OF THE PERIODIC TABLE

ALKALI METALS

The metals of the main subgroup of Group one—**lithium, sodium, potassium, rubidium, cesium, and francium**—are called **alkali metals**. This name is associated with the fact that the hydroxides of the two main representatives of this group—sodium and potassium—have long been known under the name of **alkalies**. H. Davy in 1807 was the first to obtain free potassium and sodium from these alkalies by subjecting them to electrolysis in the molten state.

Table 8

Selected Properties of the Alkali Metals

	Li	Na	K	Rb	Cs	Fr
Configuration of outer electron layer of atom	2s ¹	3s ¹	4s ¹	5s ¹	6s ¹	7s ¹
Atomic radius, nm	0.155	0.189	0.236	0.248	0.268	0.280
Ionization energy E → E ⁺ , eV	5.39	5.14	4.34	4.18	3.89	...
Radius of ion E ⁺ , nm	0.068	0.098	0.133	0.149	0.165	0.178
Standard enthalpy of atomization of metal at 25 °C, kJ per mole of atoms	150.8	91.7	90.3	82.0	78.1	...
Density, g/cm ³	0.53	0.97	0.86	1.53	1.90	2.1-2.4
Melting point, °C	179	97.8	63.55	38.8	28.5	About 20
Boiling point, °C	1350	883	776	705	690	620
Standard electrode potential of process E ⁺ + e ⁻ = E, V	-3.045	-2.714	-2.924	-2.925	-2.923	

Alkali metal atoms have one electron in their outer electron layer. The electron layer preceding the outer one has two electrons in the lithium atom, and eight electrons in the atoms of the other alkali metals. Having only one electron that is at a considerable distance from the nucleus in their outer electron layer, atoms of these elements part with this electron quite readily, i.e. are characterized by a low ionization energy (see Table 8). The singly-charged positive ions formed have a stable electron configuration corresponding to a noble gas (the lithium ion has the configuration of a helium atom; the sodium ion, that of a neon atom, etc.). The readiness of parting with their outer electrons characterizes the elements being considered as the most typical representatives of the metals: the alkali metals exhibit especially sharply expressed metallic properties.

The identical structure not only of the outer electron layer, but also of the preceding one in the atoms of all the alkali metals except for lithium explains the greatly similar properties of these elements. At the same time, the increase in the charge of the nucleus and in the total number of electrons in an atom when going down the subgroup underlies certain differences in the properties of the elements. As in the other groups, these distinctions display themselves chiefly in an increase in the readiness of giving up valence electrons and in stronger metallic properties with a growth in the atomic number.

83. Occurrence. Preparation and Properties

Owing to their property of being very readily oxidized, the alkali metals are found in nature exclusively in the form of compounds. Sodium and potassium belong to the widespread elements: the content of each of them in the Earth's crust is about 2% (mass). Both metals are encountered in various minerals and rocks of the silicate type. Sodium chloride is contained in sea water, and also forms large deposits of rock salt in many parts of the world. The upper layers of these deposits sometimes contain quite considerable amounts of potassium, chiefly in the form of the chloride or of double salts with sodium and magnesium. But large accumulations of potassium salts having a commercial significance are encountered rarely. The most important of them are the Solikamsk deposits in the USSR, the Strassfurt deposits in the GDR, and the Alsace deposits in France. Sodium nitrate occurs in Chile. The water of many lakes contains soda. Finally, enormous amounts of sodium sulphate occur in the Kara-Bogaz-Gol Bay of the Caspian Sea, where this salt in winter is deposited in a thick layer on the bottom.

Lithium, rubidium, and cesium occur much less frequently than sodium and potassium. Lithium is encountered more often than the other two, but the minerals containing it rarely form large accu-

mulations. Rubidium and cesium are contained in small amounts in some lithium minerals.

All the known francium isotopes are radioactive and rapidly decay. The first to be discovered was the isotope ^{223}Fr ; its existence was established by the French research worker Marguerite P  rey in 1939. It is formed in the decay of actinium and is encountered in a negligible amount in nature. At present, small amounts of francium are produced artificially.

Sodium and lithium are prepared by electrolysis of melts of their compounds, potassium—by reduction from melts of KOH or KCl with sodium, and rubidium and cesium by reduction from their chlorides with calcium.

All the alkali metals crystallize into a cubic body-centred lattice. They have a metallic lustre that can be observed on freshly cut metal. In air, the shiny surface of the metal immediately becomes dull owing to its oxidation.

The alkali metals are characterized by an insignificant hardness, a low density, and low melting and boiling points. Lithium has the lowest density, and francium—the lowest melting point (see Table 8).

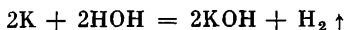
The data in Table 8 show that in the majority of cases, the properties of the alkali metals change regularly from lithium to cesium. The regularities observed are caused by the growth in the mass and radius of an atom going down the subgroup. The growth in the mass leads to a greater density. The increase in the radius underlies the weakening of the forces of attraction between the atoms, which explains the lowering of the melting and boiling points and the diminishing of the energy of atomization of the metals, and also the decrease in the ionization energy of the atoms when passing from lithium to cesium. The standard electrode potentials of the alkali metals do not change so regularly in the series Li-Cs, however. The reason, considered in detail in Vol. 1, Sec. 100, is that the values of the electrode potentials are associated with several factors that change differently when passing from one element of the subgroup to another.

The alkali metals belong to the most chemically active elements. This is due first of all to the low values of the ionization energy of their atoms—the readiness with which they part with their valence electrons. The ionization energy diminishes when going down from lithium to cesium (Table 8). It is obvious that the chemical activity grows accordingly.

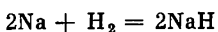
All the alkali metals combine vigorously with oxygen. Rubidium and cesium self-ignite in the air; lithium, sodium, and potassium ignite when slightly heated. It is characteristic that only lithium forms the normal oxide Li_2O in burning. The other alkali metals transform into peroxide compounds: Na_2O_2 , KO_2 , RbO_2 , and CsO_2 .

The alkali metals react no less vigorously than with oxygen with the halogens, especially with chlorine and fluorine.

The alkali metals are far ahead of hydrogen in the electromotive series and displace it from water, forming strong bases, for example:



Since they readily give up their valence electrons in chemical reactions, the alkali metals are the most vigorous reducing agents. Their reducing power is so great that they can reduce even hydrogen atoms, transforming them into negatively charged ions H^- . For instance, when alkali metals are heated in a stream of hydrogen, their hydrides are obtained, for instance:



The alkali metal hydrides have an ionic structure: the metal is the cation, and hydrogen is the anion.

Most salts of the alkali metals dissolve well in water. The salts LiF , Li_2CO_3 , Li_3PO_4 , $Na[Sb(OH)_6]$, $KClO_4$, $K_2[PtCl_6]$, $Rb_2[PtCl_6]$, $RbClO_4$, and $CsClO_4$ have a low solubility.

If we introduce a salt of an alkali metal into the flame of a gas burner, the salt decomposes, and the vapour of the liberated metal imparts a colour characteristic of the given metal to the flame. Lithium colours the flame carmine, sodium—yellow, and potassium—violet. This is how these elements can be detected in the relevant sample.

The alkali metals and their compounds are widely used in engineering. Lithium is employed in nuclear power engineering. Particularly, the isotope ${}^6Li$ is an industrial source for the production of tritium, while the isotope ${}^7Li$ is used as a heat-carrying agent in uranium reactors. Owing to the ability of lithium to readily combine with hydrogen, nitrogen, oxygen, and sulphur, it is used in metallurgy for removing traces of these elements from metals and alloys. The halides LiF and $LiCl$ are included in the fluxes used in smelting metals and welding magnesium and aluminium. Lithium and its compounds are also used as a rocket fuel. Lubricants containing lithium compounds retain their properties at temperatures from -60 to $+150^\circ C$. Lithium hydroxide is included in the composition of the electrolyte of alkaline accumulators (see Sec. 130), owing to which their service life grows from two to three times. Lithium is also employed in the ceramic, glass, and other branches of the chemical industry. In general, as regards its significance in modern engineering, this metal is one of the most important of the rare elements.

Cesium and rubidium are used in the production of photoelectric cells. These devices, which transform radiant energy into the energy of an electric current and are based on the photoelectric effect (see Vol. 1, Sec. 23), use the ability of the cesium and rubidium atoms to

detach valence electrons when radiant energy acts on one of these metals.

Sodium, potassium, and their compounds, however, find the greatest practical use.

84. Sodium (*Natrium*)

Metallic sodium is produced by the electrolysis of molten sodium chloride to which calcium chloride has been added to lower the melting point.

In the molten state, sodium and calcium chlorides mix unlimitedly, while in the solid state they are insoluble in each other. Accordingly, a simple phase diagram having a eutectic similar to that shown in Fig. 43 (p. 214) corresponds to the system NaCl-CaCl₂. The eutectic mixture of sodium and calcium chlorides melts at 505 °C, which is almost 300 °C lower than the melting point of NaCl.

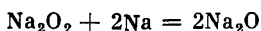
Sodium is a silvery metal. It is so soft that it can easily be cut with a knife. Since it is readily oxidized in the air, sodium is kept under a layer of kerosene.

The most important fields of application of sodium are atomic power engineering, metallurgy, and organic synthesis. In atomic power engineering, sodium and its alloy with potassium are used as liquid metal heat-carrying agents. An alloy of sodium with potassium containing 77.2% (mass) of the latter is in the liquid state within a broad range of temperatures (its melting point is -12.8 °C), has a high heat-transfer coefficient, and does not react with most structural materials at ordinary or elevated temperatures. In metallurgy, the sodium-thermal method is used to produce a number of refractory metals, and potassium is recovered by reducing KOH with sodium. Sodium is also used as an addition imparting a greater strength to lead alloys. In the industry of organic synthesis, sodium is used in the preparation of many substances. It is also employed as a catalyst in the production of certain organic polymers.

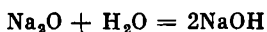
Sodium forms a solid alloy with mercury—sodium amalgam. The latter is sometimes used as a milder reducing agent instead of pure sodium.

The most important compounds of sodium with oxygen are the oxide Na₂O and the peroxide Na₂O₂.

Sodium oxide Na₂O can be prepared by passing a moderate amount of oxygen heated to not over 180 °C over sodium or by heating sodium peroxide with metallic sodium:



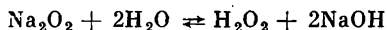
Sodium oxide reacts vigorously with water to form sodium hydroxide, with the liberation of a large amount of heat:



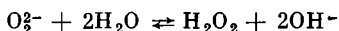
Sodium peroxide Na_2O_2 forms when sodium is burned in air or in oxygen. In industrial conditions, sodium peroxide is produced by heating molten sodium in a stream of air devoid of CO_2 . The product has a slightly yellow colour due to an admixture of the compound NaO_2 known as **sodium superoxide**.

Sodium peroxide is a very strong oxidizing agent. Many organic substances ignite upon contact with it.

When sodium peroxide is carefully dissolved in cold water, a solution is obtained that contains sodium hydroxide and hydrogen peroxide. The reaction of sodium peroxide with water is the hydrolysis of a salt formed by a weak acid—hydrogen peroxide—and a strong base— NaOH :

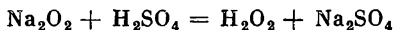


or

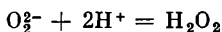


If the solution obtained is heated, oxygen evolves from it because of the decomposition of the hydrogen peroxide.

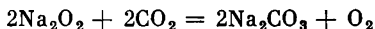
When sodium peroxide is reacted with dilute acids, hydrogen peroxide is also obtained, for instance:



or



Sodium peroxide is used to bleach fabrics, wool, silk, etc. Of great significance is the reaction between sodium peroxide and carbon dioxide:



This reaction underlies the use of sodium peroxide for the regeneration of the air in isolated premises.

Sodium hydroxide NaOH forms solid white crystals melting at 320°C , which are very hygroscopic. Owing to its strong corroding action on fabrics, leather, paper, and other organic substances, it is also called **caustic soda**.

Sodium hydroxide dissolves in water with the evolution of a large amount of heat because of the formation of various hydrates.

Sodium hydroxide must be kept in well-closed vessels because it readily absorbs carbon dioxide from the air and gradually transforms into sodium carbonate.

The main way of producing sodium hydroxide is the electrolysis of an aqueous sodium chloride solution, during which the hydrogen ions are discharged at the cathode. Simultaneously, sodium ions and hydroxide ions accumulate near the cathode, i.e. sodium hydroxide is obtained. Chlorine is liberated at the anode. It is very important to prevent mixing of the electrolysis products because sodium hydroxide readily reacts with chlorine, the result being sodium chloride

and hypochlorite:



To prevent the penetration of the chlorine into the sodium hydroxide solution, the **diaphragm method** is used most frequently: the anode and cathode spaces are separated from each other by a partition (diaphragm) made from asbestos or another porous material. In the electrolyzers used to produce sodium hydroxide according to this method (Fig. 50), vertically installed diaphragm 1 tightly adhering to steel perforated cathode 2 separates anode space 3 from cathode space 4 and prevents mixing of the electrolysis products. Graphite rods 5 are the anodes. In electrolysis, a sodium chloride solution is fed continuously into the anode space, while a solution containing a mixture of sodium chloride and hydroxide flows out of the cathode space. When it is evaporated, sodium chloride crystallizes out, and an almost pure solution of the hydroxide remains. The latter is separated from the sodium chloride and is evaporated to remove all the water. The produced NaOH is melted and cast into moulds. The by-products in the production of sodium hydroxide by this method are chlorine and hydrogen.

Electrolysis of a sodium chloride solution proceeds somewhat differently if metallic mercury is the cathode. The overvoltage of hydrogen liberation on mercury is very high. Consequently, sodium ions become discharged at the cathode instead of hydrogen ions. The liberated sodium dissolves in the mercury and forms sodium amalgam. The latter is decomposed with hot water, the products being sodium hydroxide, hydrogen, and mercury. Hence, by using mercury as the cathode, one can obtain pure sodium hydroxide containing no admixtures of sodium chloride.

Sometimes an older method is also used to produce sodium hydroxide—boiling of a soda solution with slaked lime:

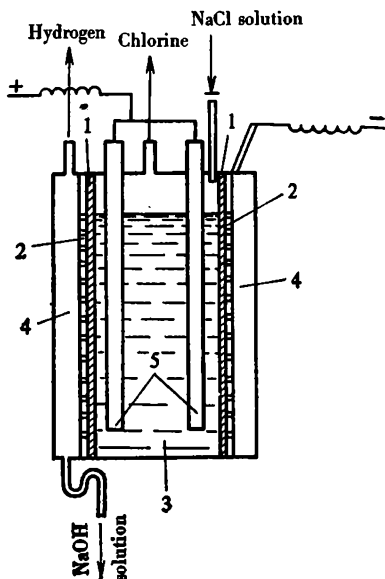
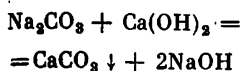


Fig. 50. Electrolyzer with a vertical diaphragm:

1—diaphragm; 2—cathode;
3—anode space; 4—cathode
space; 5—anodes

Upon completion of the reaction, the solution is poured off the calcium carbonate precipitate, and after evaporation of the water, the sodium hydroxide obtained is melted.

Sodium hydroxide is one of the most important products of the fundamental chemical industry. It is used in large amounts for purifying the products of petroleum reforming. Sodium hydroxide is widely employed in the soap, paper, textile, and other branches of industry, and also in the production of artificial fibre.

Only in the USSR, the amount of NaOH produced in 1977 was 2.7 million tonnes.

Sodium forms salts with all known acids. The most important of them were described in considering the properties of the relevant acids. Many sodium salts form crystal hydrates with quite a large content of water of crystallization (for instance, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$).

In the human organism, sodium in the form of its soluble salts, chiefly the chloride, phosphate, and hydrogen carbonate, is contained mainly in the extracellular liquids—blood plasma, lymph, and digestive juices. The osmotic pressure of the blood plasma is kept at the required level first of all by means of sodium chloride.

85. Potassium (*Kalium*)

Potassium is very similar to sodium in its appearance and in its physical and chemical properties, but is even more active. Like sodium, it is silvery in colour, oxidizes rapidly in the air, and vigorously reacts with water to evolve hydrogen.

Potassium hydroxide, or caustic potash, KOH, is produced similarly to sodium hydroxide—by the electrolysis of a potassium chloride solution. Although its action is the same as that of sodium chloride, it is used much less frequently because of its higher cost.

Potassium salts are very similar to those of sodium, but usually separate from solutions without any water of crystallization.

Potassium belongs to the elements needed in a considerable amount for plant growth. Although the soil contains quite a lot of potassium salts, a lot of them are also removed from it by certain cultured plants. Flax, hemp, and tobacco carry off an especially great amount of potassium from the soil.

Potassium is deposited chiefly in the stalks of plants, therefore, fertilization of the soil with manure containing straw partly makes up for the loss of potassium. But since the stalks of the plants listed above are used for industrial purposes, in the long run the major part of the potassium is removed from the soil, and potassium fertilizers have to be introduced into it to compensate for these losses.

The sources of potassium fertilizers are natural deposits of potassium salts. In the USSR, such deposits have been found near Soli-

kamsk. Salt layers consisting chiefly of the minerals **carallite** $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and **sylvinite** $\text{KCl} \cdot \text{NaCl}$ occur over a large area between the upper reaches of the Kama River and the foothills of the Ural mountains. In the USSR, potassium deposits also occur in the Saratov Region and in the Western Ukraine. With respect to its reserves of potassium salts, the USSR occupies the first place in the world.

Both natural substances and the products of their processing are used as potassium fertilizers. Of the natural substances, sylvinite is chiefly used. Potassium chloride and sulphate are the products of processing in the greatest favour. Sometimes plant ash containing potassium chiefly in the form of the carbonate is also used.

Like sodium, potassium forms salts with all the acids. The most important of them were treated in describing the properties of the relevant acids.

Like sodium, potassium is contained in all the tissues of the human organism. But unlike sodium, the overwhelming amount of the potassium is within the cells. The potassium ion plays an important role in certain physiological and biochemical processes, for instance, it participates in the conducting of nerve pulses. A definite concentration of potassium in the blood is needed for normal functioning of the heart. Potassium is introduced into an organism mainly with fruits and vegetables. The daily requirement of an adult in potassium is two or three grams.

COPPER SUBGROUP

The copper subgroup includes three elements—**copper**, **silver**, and **gold**. Like the alkali metal atoms, the atoms of all these elements have one electron in their outer layer; but unlike the alkali metal atoms, the preceding electron layer contains eighteen electrons. The configuration of the two outer electron layers of the atoms of these elements can be depicted by the formula $(n-1)s^2(n-1)p^2(n-1)d^{10}ns^1$ (where n is the number of the period containing the given element). All the elements of the copper subgroup are the next-to-last members of decades of d elements. As can be seen from the above formula, however, their atoms contain 10 electrons instead of 9 in the $(n-1)d$ sublevel. The explanation is that the configuration $(n-1)d^{10}s^1$ is more stable than $(n-1)d^9s^2$ (see Vol. 1, p. 102).

Table 9 gives selected physical constants characterizing the elements of the copper subgroup.

Comparing the data of Table 9 with the relevant quantities for the alkali metals (Table 8), we can see that the atomic radii of copper, silver, and gold are smaller than those of the main subgroup metals. This underlies the considerably greater density, higher melting points, and greater values of the enthalpy of atomization of the metals

Table 9

Selected Properties of Copper and Its Analogues

	Cu	Ag	Au
Configuration of outer and preceding electron layers of atom	$3s^2 3p^6 3d^{10} 4s^1$	$4s^2 4p^6 4d^{10} 5s^1$	$5s^2 5p^6 5d^{10} 6s^1$
Atomic radius, nm	0.128	0.144	0.144
Ionization energy $E \rightarrow E^+$, eV	7.73	7.57	9.23
Radius of ion E^+ , nm	0.098	0.113	0.137
Standard enthalpy of atomization of metal at 25 °C, kJ per mole of atoms	339	286	354
Density, g/cm ³	8.96	10.5	19.3
Melting point, °C	1083	960.5	1063
Boiling point, °C	2543	2167	2880
Standard electrode potential of process $E^+ + e^- = E$, V	0.520	0.799	1.692

being considered. Atoms with a smaller size are arranged more compactly in the lattice, owing to which the forces of attraction between them are large.

The small atomic radii also explain the higher values of the ionization energy of the metals of this subgroup than of the alkali metals. This leads to great differences in the chemical properties of the metals of both subgroups. The elements of the copper subgroup are metals with a low activity. They are oxidized with difficulty, and, conversely, their ions are readily reduced. They do not decompose water, and their hydroxides are comparatively weak bases. They are below hydrogen in the electromotive series. At the same time, the eighteen-electron layer, which is stable in other elements, is not yet completely stabilized here and is capable of parting with some of the electrons. For instance, copper in addition to singly-charged cations forms doubly-charged ones, which are even more characteristic of it. In exactly the same way, the oxidation number +3 is more characteristic of gold than +1. The oxidation number of silver in its ordinary compounds is +1, but compounds with an oxidation number of +2 and +3 are known.

86. Copper (*Cuprum*)

The total content of copper in the Earth's crust is comparatively small [0.01% (mass)] but it occurs more frequently than other metals in the native state, the copper nuggets reaching a considerable size. This, and also the comparative easiness of working copper, explains its use by man before other metals.

At present, copper is produced from its ores. The latter, depending on the nature of the compounds in them, are grouped into oxide and sulphide ores. Sulphide ores are of the greatest importance because they yield 80% of all the copper produced.

The most important minerals contained in copper ores are **chalcocite** or **copper glance**, Cu_2S ; **chalcopyrite** or **copper pyrite**, CuFeS_2 ; and **malachite** $(\text{CuOH})_2\text{CO}_3$.

In the USSR, rich deposits of copper ores occur in the Urals, Kazakhstan, and the Transcaucasus.

Copper ores, as a rule, contain a large amount of barren rock, so that the direct extraction of copper from them is not economical. This is why an especially important role is played in the metallurgy of copper by concentration (usually by flotation), which makes it profitable to use ores having a low copper content.

The smelting of copper from its sulphide ores or concentrates is a complicated process. It usually includes the operations of roasting, melting, converting, and fire and electrolytic refining. In the course of roasting, the major part of the sulphides of impurity elements is converted to oxides. For instance, the main impurity of most copper ores—pyrite FeS_2 —is converted to Fe_2O_3 . The flue gases in roasting contain SO_2 and are used to produce sulphuric acid.

The oxides of iron, zinc, and other impurities obtained in roasting separate in the form of a slag in melting. The main product of melting—molten matte (Cu_2S with an admixture of FeS) is fed into a converter where air is blown through it. In the course of conversion, sulphur dioxide evolves, and raw or blister copper is obtained.

To extract the valuable satellites (Au, Ag, Te, etc.) and to remove the harmful impurities, the blister copper is subjected to fire, and then electrolytic, refining. In fire refining, the molten copper is saturated with oxygen. The admixtures of iron, zinc, and cobalt are oxidized, transferred into slag, and withdrawn. The copper is poured into moulds. The castings obtained are used as the anodes in electrolytic refining (see Vol. 1, Sec. 103).

Pure copper is a ductile tenacious metal of a light pink colour that is easily rolled into thin sheets. It is an excellent conductor of heat and electricity, being inferior in this respect only to silver. Copper does not virtually change in dry air because a fine film of oxides (imparting a darker colour to the metal) forms on its surface and affords good protection against further oxidation. But in the presence of moisture and carbon dioxide, the surface of copper becomes coated with a greenish deposit of copper carbonate hydroxide $(\text{CuOH})_2\text{CO}_3$. When heated in the air within the temperature range from 200 to 375 °C, copper oxidizes to black copper(II) oxide CuO . At higher temperatures, a double-layer scale appears on its surface: the top layer is copper(II) oxide, and the internal layer is red copper(I) oxide Cu_2O .

Its high thermal and electrical conductivity, ductility, excellent casting properties, high tensile strength, and chemical stability have brought copper into great demand in industry.

Large amounts of pure electrolytic copper (about 40% of all the copper produced) go to make electrical wires and cables. A variety of industrial equipment such as boilers, evaporation tanks, and stills is made from copper.

Various alloys of copper with other metals have found broad application in the machine-building industry, as well as in electrical engineering and other branches of industry. The most important copper alloys are **brasses** (alloys of copper with zinc), **copper-nickel** alloys, and **bronzes**.

Brass contains up to 45% zinc. **Simple** and **special** brasses are distinguished. The latter, in addition to copper and zinc, include other elements, for instance iron, aluminium, tin, and silicon. Brass finds diverse applications. It is used to make tubes for condensers and radiators, components of mechanisms, particularly of clocks and watches. Some special brasses have a high resistance to corrosion in sea water and are used in ship-building. Brass with a high copper content—**tombac**—owing to its appearance being similar to that of gold is used to make decorative articles and cheap jewelry.

Copper-nickel alloys are grouped into structural and electrotechnical ones. The structural alloys include **cupronickels** and **nickel silvers**. Cupronickels contain 20-30% nickel and small amounts of iron and manganese, while nickel silvers (formerly called German silvers) contain 5-35% nickel and 13-45% zinc. Owing to their resistance to corrosion in water, including sea water, the structural copper-nickel alloys have come into great favour in ship-building and power engineering. They are used to make radiators, pipes, and distillation equipment for preparing potable water from sea water. The electrotechnical copper-nickel alloys include **constantan** (40% Ni and 1.5% Mn) and **manganin** (3% Ni, 12% Mn) having a low temperature coefficient of electrical resistance and used to manufacture resistance boxes, and also the alloy **Copel** (43% Ni and 0.5% Mn) which thermocouples are made from.

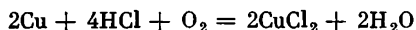
Bronzes are grouped according to their main component (in addition to copper) into tin, aluminium, silicon, and other bronzes. Tin bronzes are the most ancient. For many centuries, they occupied a leading place in many branches of production. At present, their use in machine-building is falling off. Greater favour is being given to aluminium bronzes (5-10% Al and additions of Fe, Mn, and Ni). Beryllium bronzes are very strong and go to make springs and other vital components.

All copper alloys have a high resistance to atmospheric corrosion.

Chemically, copper is a metal with a low activity. With the halogens, however, it reacts even at room temperature, for instance with

moist chlorine it forms the chloride CuCl_2 . The reaction of copper with the oxygen of the air was mentioned above. When heated, copper also reacts with sulphur to form the sulphide Cu_2S .

Being in the electromotive series below hydrogen, copper does not displace it from acids. Consequently, hydrochloric and dilute sulphuric acids do not react with copper. But in the presence of the oxygen of the air, copper dissolves in these acids to form the relevant salts:



Volatile copper compounds colour the non-luminous flame of a gas burner bluish green.

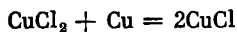
Compounds are known in which copper has the oxidation numbers one, two, and three. They can be considered as derivatives of the relevant oxides: Cu_2O , CuO , and Cu_2O_3 .

The compounds of copper(I) are in general less stable than those of copper(II). The oxide Cu_2O_3 and its derivatives are very unstable.

Copper(I) Compounds. *Copper(I) oxide* Cu_2O occurs in nature in the form of the mineral *cuprite*. It can be prepared artificially by heating a solution of a copper(II) salt with an alkali and a strong reducing agent such as formalin or glucose. A precipitate of red copper(I) oxide is formed.

Paired with metallic copper, Cu_2O is used in alternating-current copper-oxide rectifiers.

When Cu_2O is reacted with hydrogen chloride, a colourless solution of *copper(I) chloride* CuCl is obtained. If the solution is diluted with water, the copper(I) chloride precipitates as white curds insoluble in water. It can also be prepared by boiling a solution of copper(II) chloride CuCl_2 with metallic copper in a hydrochloric acid solution:



Copper(II) Compounds. *Copper(II) oxide* CuO is a black substance encountered in nature (for instance, in the form of the mineral *tenorite*). It can easily be prepared by roasting copper(II) carbonate hydroxide $(\text{CuOH})_2\text{CO}_3$ or copper(II) nitrate $\text{Cu}(\text{NO}_3)_2$. Copper(II) oxide exhibits oxidizing properties. When heated with various organic substances, CuO oxidizes them, converting the carbon to carbon dioxide and the hydrogen to water, becoming reduced itself to metallic copper. This reaction is used in the elementary analysis of organic substances to determine their carbon and hydrogen contents.

Copper(II) hydroxide $\text{Cu}(\text{OH})_2$ precipitates from solutions of copper(II) salts as a light blue jelly under the action of alkalis. When slightly heated even under water, it decomposes, transforming into black copper(II) oxide.

Copper(II) hydroxide is a very weak base. Therefore, solutions of copper(II) salts usually have an acid reaction, while with weak acids copper forms basic salts.

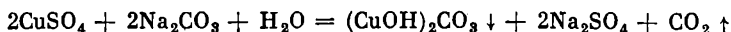
The following are the most important of the copper(II) salts.

Copper(II) sulphate CuSO_4 in the anhydrous state is a white powder that turns blue when it absorbs water. It is therefore used to detect traces of moisture in organic liquids. An aqueous solution of copper(II) sulphate has a characteristic light blue colour. This colour is a property of the hydrated ions $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$, consequently all dilute solutions of copper(II) salts have the same colour if they contain no coloured anions. Copper sulphate crystallizes from aqueous solutions with five molecules of water to form transparent blue crystals (**blue vitriol**, see p. 58).

Copper(II) chloride $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ forms dark green crystals readily soluble in water. Highly concentrated solutions of copper(II) chloride have a green colour, and dilute solutions—a bluish green one.

Copper(II) nitrate $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ is produced when copper is dissolved in nitric acid. When heated, the blue crystals of copper(II) nitrate first lose their water, and then readily decompose with the evolution of oxygen and brown nitrogen dioxide, transforming into copper(II) oxide.

Copper(II) carbonate hydroxide $(\text{CuOH})_2\text{CO}_3$ occurs in nature as the mineral malachite having a beautiful emerald-green colour. It is prepared artificially by reacting Na_2CO_3 with solutions of copper(II) salts:



It is used for preparing copper(II) chloride, for producing blue and green mineral paints, and also in pyrotechnics.

Copper(II) acetate $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ is prepared by reacting metallic copper or copper(II) oxide with acetic acid. It is usually a mixture of basic salts of various composition and colour (green and blue-green). It is used under the name of **verdigris** for the preparation of oil paints.

Double copper(II) acetate-arsenite $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{Cu}_3(\text{AsO}_3)_2$ is used under the name **Paris green** for destroying plant pests.

Copper salts are employed to produce a large amount of mineral paints differing in colour: green, blue, brown, violet, and black. *All copper salts are poisonous.* This is why copper utensils are **tinned**, i.e. coated inside with tin to prevent the formation of copper salts.

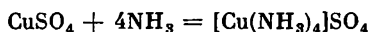
Complex Compounds of Copper. A characteristic property of doubly-charged copper ions is their ability to combine with ammonia molecules to form **complex ions**.

If we pour an ammonia solution into a solution of copper sulphate, a blue precipitate of the basic salt is formed that readily dissolves in

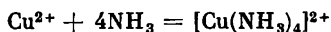
an excess amount of ammonia and colours the liquid an intense blue. The addition of an alkali to the solution obtained does not cause a precipitate of copper hydroxide $\text{Cu}(\text{OH})_2$ to appear. Hence, this solution contains so few Cu^{2+} ions that even with a large amount of OH^- ions the solubility product of $\text{Cu}(\text{OH})_2$ is not reached. We can thus conclude that the copper ions react with the ammonia to form new ions that do not produce an insoluble compound with the OH^- ions. At the same time, the SO_4^{2-} ions remain unchanged because the addition of barium chloride to the ammonia solution immediately results in the formation of a barium sulphate precipitate (the characteristic reaction for the SO_4^{2-} ion).

Investigations have shown that the dark blue colour of the ammonia solution is due to the presence in it of the complex ions $[\text{Cu}(\text{NH}_3)_4]^{2+}$ formed by the attachment of four ammonia molecules to a copper ion. When the water is evaporated, the ions $[\text{Cu}(\text{NH}_3)_4]^{2+}$ combine with the SO_4^{2-} ions, and dark blue crystals separate from the solution whose composition is expressed by the formula $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$.

Hence, the reaction of copper(II) sulphate with ammonia is as follows:



or in the net ionic form:

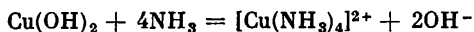


Ions that like $[\text{Cu}(\text{NH}_3)_4]^{2+}$ are formed by the attachment of neutral molecules or ions of the opposite sign to a given ion are called complex ions. Salts containing such ions have been named complex salts. Complex acids, complex bases, and complex non-electrolytes are also known.*

When writing formulas, a complex ion is generally confined in brackets. This indicates that upon dissolution of a given compound in water, the complex ion does not virtually dissociate.

Like copper(II) sulphate, other salts of divalent copper also react with ammonia. In all these cases, dark blue solutions containing the complex ions $[\text{Cu}(\text{NH}_3)_4]^{2+}$ are obtained.

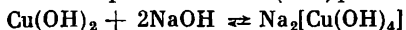
Copper(II) hydroxide also dissolves in ammonia with the formation of a dark blue solution containing the ions $[\text{Cu}(\text{NH}_3)_4]^{2+}$



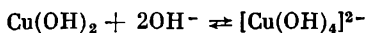
The solution obtained can dissolve cellulose (cotton wool, filter paper, and the like) and is employed in the production of one of the kinds of artificial fibre (see p. 166).

* This definition of complex compounds is not exhaustive. These compounds will be treated in greater detail in Chapter 8.

Copper(II) hydroxide also dissolves in very concentrated solutions of alkalis to form bluish violet solutions of **cuprites**—salts containing the complex ion $[\text{Cu}(\text{OH})_4]^{2-}$:

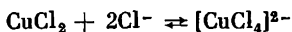


or in the net ionic form:

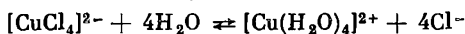


Unlike the ammonia complexes of copper, in this case the copper ion attaches OH^- ions instead of neutral molecules, and as a result **complex anions** are formed, and not cations. Cuprites are very unstable, and when alkaline solutions are diluted with water they decompose with copper(II) hydroxide precipitating.

Among other complex copper(II) anions, we must mention the $[\text{CuCl}_4]^{2-}$ ions formed in concentrated copper(II) chloride solutions and colouring them green:



When the solutions are diluted with water, the $[\text{CuCl}_4]^{2-}$ ions transform into ordinary hydrated copper ions $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ and the green solutions turn light blue:



Copper is one of the **microelements**. This name was given to Fe, Cu, Mn, Mo, B, Zn, and Co because small amounts of them are needed for the normal vital activity of plants. Microelements increase the activity of enzymes, facilitate the synthesis of sugar, starch, proteins, nucleic acids, vitamins, and enzymes. Microelements are introduced into the soil with **microfertilizers**. Fertilizers containing copper promote the growth of plants on certain poor soils, and improve their resistance to droughts, cold, and some diseases.

87. Silver (*Argentum*)

Silver is much less abundant in nature than copper. Its content in the Earth's crust is only $10^{-5}\%$ (mass). Native silver is found in some places (for example, in Canada), but the major part of silver is obtained from its compounds. The most important silver ore is **silver glance**, or **argentite**, Ag_2S .

Silver is present as an admixture in almost all copper and especially lead ores. These ores yield about 80% of all the silver produced.

In the USSR, silver is extracted chiefly from silver lead ores whose deposits have been found in the Urals, the Altai, the Northern Caucasus, and Kazakhstan.

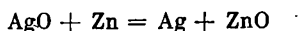
Pure silver is a very soft ductile metal. It is the best conductor of heat and electricity among all the metals.

Silver finds virtually no use in practice owing to its softness. It is usually alloyed with a certain amount of copper. Silver alloys are

employed in the production of jewelry and domestic articles, coins, and laboratory utensils*. Silver is used to coat other metals, and also radio components for increasing their electrical conductance and resistance to corrosion. Part of the silver produced goes to make silver-zinc accumulators.

In silver-zinc accumulators distinguished by their good electrical characteristics and having a low mass and volume, the electrodes are silver oxides Ag_2O and AgO (the cathode), and spongy zinc (the anode). A KOH solution is the electrolyte.

In operation of the accumulator, the zinc oxidizes and transforms into ZnO and Zn(OH)_2 , while the silver oxide is reduced to the metal. The net reaction proceeding in the discharge of an accumulator can be expressed approximately by the equation:



The e.m.f. of a charged silver-zinc accumulator is about 1.85 V. When the voltage drops to 1.25 V, the accumulator is charged, the reverse processes occurring at the electrodes: the zinc is reduced, and the silver is oxidized—the substances needed for operation of the accumulator are again obtained.

Silver is a metal with a low activity. It does not oxidize in atmospheric air at room temperature or when heated. The frequently observed blackening of silver objects is the result of the formation of black silver sulphide Ag_2S on their surface. This occurs under the influence of the hydrogen sulphide contained in the air (see p. 52), and also when silver objects come into contact with food products containing sulphur compounds.

Silver is considerably below hydrogen in the electromotive series. Therefore, hydrochloric and dilute sulphuric acids do not react with it. Silver is usually dissolved in nitric acid, the reaction following the equation:



Silver forms one series of salts whose solutions contain the colourless cations Ag^+ .

Silver(I) Oxide Ag_2O . When alkalis react with solutions of silver salts, the expected product is AgOH , but instead of it a brown precipitate of silver(I) oxide is formed:



* The silver or gold content in an alloy is indicated by a **standard fineness number** branded on the articles made from it (**hallmarks**). In the Soviet Union, a metric system of standard fineness numbers is used. The numbers show how many units of mass of the precious metal are contained in 1000 units of the alloy. In Great Britain, the USA, and some other countries, the carat system is used, the standard for pure metal being 24 carats.

The most widespread are silver articles of the standard fineness numbers 800 and 875 (19.2 and 21 carats) and gold ones of the numbers 583 and 750 (14 and 18 carats).

Silver(I) oxide dissolves insignificantly in water (0.017 g/l). The obtained solution has an alkaline reaction and, like alkalis, precipitates the hydroxides of some metals from solutions of their salts. The solution evidently contains silver hydroxide AgOH , which is a quite strong base. The latter is confirmed by the fact that silver salts do not become hydrolyzed.

In addition to silver(I) oxide, the oxides AgO and Ag_2O_3 are known.

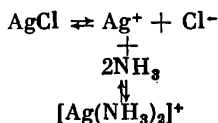
The following silver salts are the most important ones.

Silver nitrate AgNO_3 , also known as **lunar caustic**. It forms colourless crystals that dissolve well in water. It is used in the production of photographic materials, in the manufacture of mirrors, in electroplating, and in medicine.

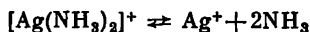
Silver chloride AgCl forms as white curds insoluble in water and in acids when silver ions react with chloride ions. Silver chloride gradually darkens in the light, decomposing with the liberation of metallic silver. **Silver bromide** and **iodide** have similar properties, but unlike silver chloride they have a yellow colour. In contrast to the other silver halides, silver fluoride AgF is soluble in water.

Complex Compounds of Silver. Like copper, silver is disposed to form complex compounds.

Many silver compounds that are insoluble in water, for instance silver(I) oxide and silver chloride, readily dissolve in an aqueous solution of ammonia. The explanation is the formation of the complex ions $[\text{Ag}(\text{NH}_3)_2]^+$. For example, the equilibria setting in when silver chloride reacts with an aqueous solution of ammonia can be represented as follows:



In a saturated solution of silver chloride, dynamic equilibrium sets in between the Ag^+ and Cl^- ions and the AgCl precipitate. The ammonia molecules introduced into the solution combine with the silver ions to form the complex ions $[\text{Ag}(\text{NH}_3)_2]^+$, and the precipitate dissolves. Hence, silver is in an ammonia solution in the form of the complex cations $[\text{Ag}(\text{NH}_3)_2]^+$. But in addition to them, there always remains in the solution a certain, although insignificant, amount of silver ions owing to dissociation of the complex ion according to the equation:



Complex cyanic compounds of silver are used for galvanic silver plating because upon the electrolysis of solutions of these salts a dense layer of finely crystalline silver is deposited on the surface of ar-

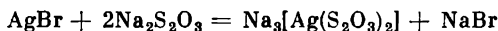
ticles. When a current is passed through a solution of $K[Ag(CN)_2]$, silver is deposited at the cathode at the expense of an insignificant amount of silver ions obtained owing to dissociation of the complex anion:



All silver compounds are readily reduced with the liberation of metallic silver. When a small amount of glucose or formalin is added as a reducing agent to an ammonia solution of silver(I) oxide in a glass vessel, metallic silver is deposited as a dense shiny mirror layer on the surface of the glass. This is how mirrors are manufactured, and the internal surface of the glass in Dewar flasks and thermos bottles is coated with silver to diminish the heat losses by radiation.

Silver salts, especially the chloride and bromide, owing to their ability of decomposing under the influence of light with the liberation of metallic silver, are widely used in the production of photographic materials—films, paper, and plates. These materials generally consist of a light-sensitive suspension of $AgBr$ in gelatin, a layer of which is applied to Celluloid, paper, or glass.

Upon an **exposure**, at the portions of a light-sensitive layer acted upon by light, very minute seeds of metallic silver crystals are formed. This is a latent image of the object being photographed. In **developing**, the silver bromide decomposes, the rate of decomposition being higher with increasing concentration of the seeds at a given spot of the layer. A visible image is obtained that is an inverted or **negative** image because the degree of blackening at each spot of the light-sensitive layer is greater when it was illuminated more during the exposure. Next, **fixing** is performed to remove the undecomposed silver bromide from the light-sensitive layer. This occurs as a result of a reaction between the $AgBr$ and the sodium thiosulphate contained in the fixing salt. The products include a soluble complex salt and sodium bromide:



The negative is then projected or placed onto photographic paper (in red light, which does not act on silver bromide), and the latter is exposed by passing light through the negative ("printing"). More light passes through the negative where it is lighter. Hence, in the course of printing, the relation between light and shadows is reversed and now corresponds to the photographed object. This is a **positive** image.

Silver ions suppress the development of bacteria and sterilize potable water even at a very low concentration (about 10^{-10} mol/l). In medicine, colloidal solutions of silver (protargolum, collargolum, etc.) stabilized with special additions are used for disinfection of the mucous membranes.

88. Gold (*Aurum*)

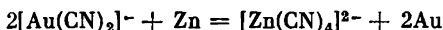
Gold occurs in nature almost exclusively in the native state, chiefly as fine grains embedded in quartz or contained in quartz sand. Small amounts of gold are encountered in the sulphide ores of iron, lead, and copper. Traces of it have been discovered in sea water. The total gold content in the Earth's crust is only $5 \times 10^{-7}\%$ (mass).

In the USSR, gold deposits are found in Siberia and the Urals. There are major gold deposits in South Africa, Alaska, Canada, and Australia.

Gold is separated from sand and crushed quartz rock by washing with water that carries off the lighter sand particles, or by treatment with liquids that dissolve the gold. Most often, a solution of sodium cyanide NaCN is used in which gold dissolves in the presence of oxygen with the formation of the complex anions $[\text{Au}(\text{CN})_2]^-$:



Gold is recovered from the solution obtained with zinc:



The precipitated gold is treated with dilute sulphuric acid to separate the zinc from it, is washed and dried. The gold is further purified of impurities (mainly of silver) by treating it with hot concentrated sulphuric acid or by electrolysis.

The method of winning gold from its ores by means of potassium or sodium cyanide solutions was developed in 1843 by the Russian engineer P. Bagration. This method, which is a hydrometallurgical method of extracting metals, at present has found its greatest application in the metallurgy of gold.

Gold is a bright yellow lustrous metal. It is very malleable and ductile and can be rolled into sheets less than 0.0002 mm thick. A wire 3.5 kilometres long can be drawn from one gram of gold. Gold is an excellent conductor of heat and electricity and is inferior in this respect only to silver and copper.

Owing to its softness, gold is generally alloyed with silver or copper. These alloys are used for electrical contacts, for artificial teeth, and in jewelry (see the footnote on p. 246).

Chemically, gold has a low activity. It does not change in the air even when strongly heated. Acids when taken separately do not react with gold, but it readily dissolves in a mixture of hydrochloric and nitric acids (aqua regia). It also dissolves readily in chlorine water and in aerated solutions of alkali metal cyanides. Mercury also dissolves gold and forms an amalgam which becomes solid when it contains over 15% gold.

Two series of gold compounds are known corresponding to the oxidation numbers +1 and +3. For instance, gold forms two oxides—gold(I) oxide Au_2O and gold(III) oxide Au_2O_3 . The compounds in which gold has an oxidation number of +3 are more stable.

When gold dissolves in aqua regia, a complex is formed called **chloroauric acid** $\text{H[AuCl}_4\text{]}$. It crystallizes as light yellow needles having the composition $\text{H[AuCl}_4\text{]} \cdot 4\text{H}_2\text{O}$ (the usual commercial gold preparation). Well crystallizing salts of this acid are known, for example $\text{Na[AuCl}_4\text{]}$, in whose solutions gold is in the form of the complex anion $[\text{AuCl}_4]^-$.

If chloroauric acid is carefully heated, it decomposes with the liberation of HCl and reddish brown crystals of **gold(III) chloride** AuCl_3 .

Alkalies precipitate from solutions of chloroauric acid brown gold(III) hydroxide Au(OH)_3 , also known as **auric acid** because this substance has weakly acidic properties and forms salts. At 100°C , auric acid loses water and transforms into the red gold(III) oxide Au_2O_3 .

When gold(III) chloride is heated in a stream of carbon dioxide to 180°C , **gold(I) chloride** AuCl is obtained as a white substance insoluble in water. Alkalies precipitate the violet gold(I) oxide Au_2O from solutions of gold(I) chloride.

All gold compounds readily decompose when heated with the separation of metallic gold.

8

COMPLEX COMPOUNDS

When discussing the elements of the copper subgroup, we saw that the ions of these elements can attach other ions or neutral molecules (for instance, NH_3) and form more elaborate complex ions. When the latter combine with ions of the opposite sign, various complex compounds are obtained.

Complex compounds are the most widespread and diverse class of inorganic substances. They also include many organometallic compounds (p. 136) that combine the previously isolated inorganic chemistry and organic chemistry into a single entity. Many complex compounds—vitamin B_{12} , hemoglobin, chlorophyll, and others—play a great role in physiological and biochemical processes. The investigation of the properties and spatial structure of complex compounds was exceedingly fruitful for **crystal chemistry**, which studies the dependence of the physicochemical properties of substances on the structure of the crystals they form, and gave birth to new ideas on the nature of the chemical bond. The employment of complex compounds in analytical chemistry also led to valuable results. We shall not exaggerate if we say that the achievements of theoretical and applied chemistry in recent years are in many respects associated with the study of complex compounds.

The properties and structure of complex compounds are explained most successfully by the **coordination theory** proposed by A. Werner in 1893.



Alfred Werner (1866-1919)

Alfred Werner, a Swiss chemist, Nobel Prize winner, was one of the founders of the concept of complex compounds. Werner's scientific activities were conducted at the Zurich University, where he was a professor from 1893. He synthesized a great number of novel

complex compounds, systematized the previously known and newly prepared complex compounds, and worked out experimental methods of proving their structure. To explain the structure and properties of complex compounds, Werner advanced the idea of coordination, i.e. of a metal ion being surrounded in space by anions or neutral molecules. The coordination theory was the cornerstone of the modern notions of complex compounds.

89. Fundamentals of the Coordination Theory

According to the coordination theory, one of the ions in a molecule of any complex compound, generally a positively charged one, occupies a central position and is called a **complexing agent** or **central ion**. Around it in direct proximity are arranged, or, as we say, **coordinated**, a certain number of oppositely charged ions or electrically neutral molecules called **ligands** (or addends) and forming the **inner coordination sphere** of the compound. The remaining ions not accommodated in the inner sphere are farther from the central ion and form the **outer coordination sphere**. The number of ligands surrounding the central ion is called the **coordination number**.

The inner sphere of a complex retains its stability to a considerable extent when dissolved. Its boundaries are shown in formulas by brackets. The ions in the outer sphere are readily detached in solutions. For this reason, the ions in the inner sphere are said to have a **non-ionogenous** bond, and those in the outer sphere, an **ionogenous** one. For example, the coordination formula of the complex salt having the composition $\text{PtCl}_4 \cdot 2\text{KCl}$ is $\text{K}_2[\text{PtCl}_4]$. Here the inner sphere consists of a central platinum atom in the +4 oxidation state and chloride ions, while the potassium ions are in the outer sphere.

One must not think that complex compounds are always built up of ions; actually, the effective charges of the atoms and molecules in a complex are generally not great. It is therefore more proper to use the term "central atom". The ionic notions on the nature of the bond in complex compounds are to a certain extent formal, but they are convenient for the classification and determining of the charges of complexes, and allow some of their properties to be predicted qualitatively.

Werner's coordination theory still remains the guiding one in the chemistry of complex compounds. Only the notions of the forces acting between the central atom and the ligands change and are determined more precisely with time (see Sec. 92). The broad dissemination of this theory explains why complex compounds are often referred to as "coordination compounds".

There are a number of ways of establishing the coordination formulas of complex compounds.

With the aid of double exchange reactions. The structure of the following complex compounds of platinum was proved in this way: $\text{PtCl}_4 \cdot 6\text{NH}_3$, $\text{PtCl}_4 \cdot 4\text{NH}_3$, $\text{PtCl}_4 \cdot 2\text{NH}_3$, and $\text{PtCl}_4 \cdot 2\text{KCl}$.

If a solution of the first compound is reacted with a solution of AgNO_3 , the entire chlorine contained in it precipitates in the form of silver chloride. It is thus evident that all four chloride ions are in the outer sphere, and, consequently, the inner sphere consists only of ammonia molecules. The coordination formula of the compound will thus be $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$. In the compound $\text{PtCl}_4 \cdot 4\text{NH}_3$, silver nitrate precipitates only half of the chlorine, i.e. the outer sphere contains only two chloride ions, while the other two together with the four ammonia molecules are in the inner sphere; hence, the coordination formula is $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$. A solution of the compound $\text{PtCl}_4 \cdot 2\text{NH}_3$ gives no precipitate with AgNO_3 ; the formula of this compound is $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$. Finally, silver nitrate also precipitates no AgCl from a solution of $\text{PtCl}_4 \cdot 2\text{KCl}$, but it can be established by conducting exchange reactions that the solution contains potassium ions. On these grounds, its structure is depicted by the formula $\text{K}_2[\text{PtCl}_6]$.

With the aid of the molar conductivity of dilute solutions*. Upon great dilution, the value of the molar conductivity μ of a complex compound is determined by the charge and number of the ions formed. The following approximate relationship holds for compounds containing a complex ion and singly charged cations or anions:

Number of ions into which a molecule of the electrolyte decomposes	2	3	4	5
μ , $\Omega^{-1}\text{cm}^2 \text{mol}^{-1}$	100	250	400	500

Measurement of the electrical conductivity confirms the coordination formulas of the platinum complexes given above. Their conductivity changes as shown in Fig. 51. For the first compound, $\mu \approx 500$, which points to the formation of five ions when it dissociates and corresponds to the coordination formula $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$.

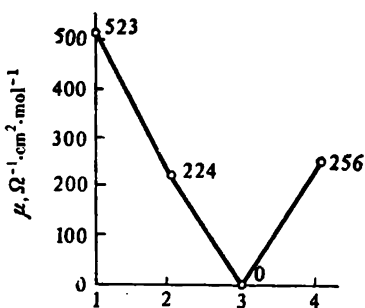


Fig. 51. Change in molar conductivity μ in series of complex platinum(IV) compounds:

- 1— $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$;
2— $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$;
3— $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$; 4— $\text{K}_2[\text{PtCl}_6]$

* The molar conductivity of a solution μ equals the conductivity of a volume of the solution containing one mole of the substance and confined between electrodes spaced 1 cm apart. The values of μ are expressed in $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$.

As the NH_3 molecules are replaced in the inner sphere with Cl^- ions, the conductivity drops and becomes the minimum for the non-electrolyte $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$. When going over to the compound $\text{K}_2[\text{PtCl}_6]$, the conductivity again grows, and its magnitude corresponds to the formation of three ions in dissociation.

With the aid of the X-ray structural method. The coordination formula of a complex compound in the crystalline state can be established directly by determining the mutual position of the atoms and molecules in a crystal by the X-ray structural method. To do this, however, it is necessary to grow a sufficiently large and undistorted crystal of the complex compound, which is not always possible. A number of other physicochemical methods can be used to establish the coordination formulas of complex compounds.

Upon analysing the coordination numbers of many complex compounds, Werner arrived at the conclusion that the charge of the central ion (or, more exactly, the oxidation number of the central atom) is the main factor affecting the coordination number. A comparison of the most characteristic coordination numbers in solutions and the charge of the central ion is given below:

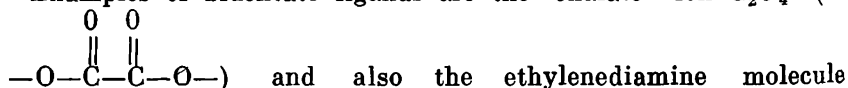
Charge of central ion	+1	+2	+3	+4
Coordination number	2	4, 6	6, 4	8

The coordination numbers encountered more often when two different kinds of coordination are possible are set here in bold-face type. The coordination number 6 is encountered in the complex compounds of Pt^{4+} , Cr^{3+} , Co^{3+} , and Fe^{3+} , the coordination number 4—in the complexes of Cu^{2+} , Zn^{2+} , Pd^{2+} , and Pt^{2+} , the coordination number 2—in the complexes of Ag^+ and Cu^+ . The above coordination numbers correspond to the maximum saturation of the coordination sphere and relate to **coordinationally saturated** compounds. The conditions essential for this are not always observed in solutions, and the result is the formation of coordinationally unsaturated complexes with smaller coordination numbers.

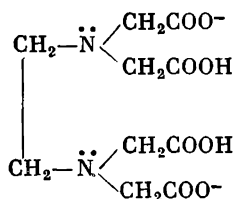
The coordination number is not a constant quantity for a given complexing agent, but also depends on the nature of the ligand and its electron properties. Even for the same complexing agents and ligands, the coordination number depends on the state of aggregation, the concentration of the components, and the temperature of the solution.

Ligands occupying one site in the inner coordination sphere are called **monodentates**. Ligands exist that occupy two or several sites in the inner sphere. They are called **bi-** and **polydentates**.

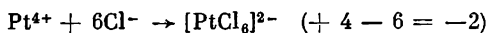
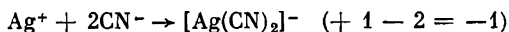
Examples of bidentate ligands are the oxalate ion $\text{C}_2\text{O}_4^{2-}$ (or



($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$). The doubly charged anion of ethylenediamine-tetraacetic acid is a tetradentate ligand:



The charge of a complex ion [equals the algebraic sum of the charges of its constituent simple ions. For example,



The electrically neutral molecules such as NH_3 , H_2O , and C_2H_4 in a complex do not affect the magnitude of its charge. Therefore, they may be left out of consideration in determining the charge of complex ions. The charge of the complexing agent, in turn, is readily found from the charge of the complex ion and the charges of the ligands in the complex.

Neutral molecules or anions in the inner sphere of a complex compound can be consecutively replaced with other molecules or anions. For example, replacement of the ammonia molecules in the complex salt $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ with NO_2^- ions yields the following compounds: $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$, $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$, $\text{K}_2[\text{Co}(\text{NH}_3)(\text{NO}_2)_5]$, and $\text{K}_3[\text{Co}(\text{NO}_2)_6]$. It is clear that such replacement is attended by a gradual change in the charge of the complex ion, which lowers from +3 in the ion $[\text{Co}(\text{NH}_3)_6]^{3+}$ to -3 in the ion $[\text{Co}(\text{NO}_2)_6]^{3-}$.

90. Basic Types and Nomenclature of Complex Compounds

The basic types of complex compounds include the following.

Ammines—complexes in which ammonia molecules are the ligands, for instance $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, and $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$. Complexes similar to the ammines are known in which the role of the ligand is played by amine molecules: CH_3NH_2 (methylamine), $\text{C}_2\text{H}_5\text{NH}_2$ (ethylamine), $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (ethylenediamine, conventionally designated En or en), etc. Such complexes are known as **aminates**.

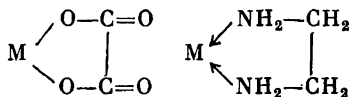
Aquacomplexes contain water as the ligand: $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$, $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, etc. Hydrated cations in an aqueous solution contain an aquacomplex as the central unit. In the crystal-

line state, some of the aquacomplexes also retain the water of crystallization, for example $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$, and $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4 \cdot \text{H}_2\text{O}$. The water of crystallization is not contained in the inner sphere. It is bonded less strongly than the coordinated water and is parted with more readily in heating.

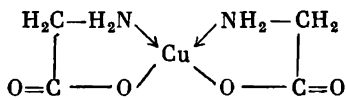
Acidocomplexes. In these complexes, anions are the ligands. They include complexes of the double salt type, for example, $\text{K}_2[\text{PtCl}_4]$, $\text{K}_4[\text{Fe}(\text{CN})_6]$ (they can be represented as the product of the coupling of two salts— $\text{PtCl}_4 \cdot 2\text{KCl}$, $\text{Fe}(\text{CN})_2 \cdot 4\text{KCN}$, etc.), complex acids— $\text{H}_2[\text{SiF}_6]$, $\text{H}_2[\text{CoCl}_4]$, hydroxocomplexes— $\text{Na}_2[\text{Sn}(\text{OH})_4]$, $\text{Na}_2[\text{Sn}(\text{OH})_6]$, etc.

Transition series exist between these classes, which include complexes with different ligands. We have already mentioned such complexes in the preceding section. Below is given the transition series between the amines and acidocomplexes of platinum(II): $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$, $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}$, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_3]$, and $\text{K}_2[\text{PtCl}_4]$.

Cyclic, or chelate (from the Greek word “chele”—claw) complex compounds contain a bi- or polydentate ligand that grips the central atom, as it were, like the claws of a crab:

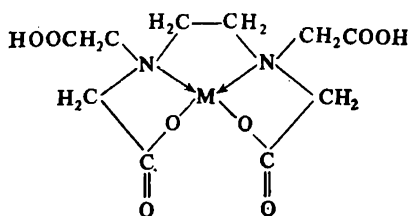


In these complexes, the symbol M stands for a metal atom, and the arrow depicts a donor-acceptor bond. Examples of such complexes are the oxalate complex of iron(III) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ and the ethylenediamine complex of platinum(IV) $[\text{PtEn}_3]^{4+}$. The group of chelates also includes **intracomplex compounds** in which the central atom is part of a ring, forming covalent bonds with ligands in various ways—donor-acceptor bonds and bonds at the expense of unpaired atomic electrons. Complexes of this kind are very characteristic of the aminocarboxylic acids. Their simplest representative is aminoacetic acid (glycine) $\text{NH}_2\text{CH}_2\text{COOH}$ —it forms chelates with Cu^{2+} , Pt^{2+} , and Rh^{3+} ions, for example:



Complexes are also known with more complicated aminocarboxylic acids and their analogues. Such ligands are known as **complexons**. The doubly charged anion of ethylenediaminetetraacetic acid (see the preceding section) in the form of its bisodium salt is called **complexon III**, or **trilon B**; it produces a complex of the following type

with a bivalent metal:



Chelate compounds are extremely stable because their central atom is "blocked", as it were, by the cyclic ligand. Chelates with five- and six-membered rings have the highest stability. Complexons bond metal cations so strongly that such poorly soluble substances as calcium and barium sulphates, calcium oxalates and carbonates dissolve when they are added. This explains their use for softening water, and for camouflaging "surplus" metal ions in the dyeing and manufacture of coloured films. They also find great application in analytical chemistry.

Many organic ligands of the chelate type are very sensitive and specific reagents for cations of the transition metals. They include, for example, dimethylglyoxime proposed by L. Chugaev as a reagent for the Ni^{2+} and Pd^{2+} ions.



Lev Aleksandrovich Chugaev
(1873-1922)

Lev Aleksandrovich Chugaev is one of the most outstanding Soviet chemists. He was born in Moscow; in 1895 he graduated from the Moscow University. In 1904-1908, he was a professor at the Moscow Higher Technical College, and in 1908-1922, a professor in inorganic chemistry at the Petrograd University, and simultaneously (from 1909) a professor in organic chemistry at the Petrograd Technological Institute. His main interests included the chemistry of complex compounds of the transition metals, especially of the platinum group metals. He discovered many new complex compounds important both theoretically and practically. He was the first to draw attention to the great

stability of five- and six-membered rings in the inner sphere of complex compounds and to characterize the acid-basic properties of platinum(IV) amines. He was one of the initiators of the use of organic reagents in

analytical chemistry. Chugaev devoted much attention to the organization and development of the platinum and platinum metal mining and processing industry in the USSR. He founded a large Soviet school of inorganic chemists working in the field of studying complex compound chemistry.

Chelate compounds also play a great role in nature. For instance, hemoglobin consists of a complex—heme—bonded to a protein—globin. The central ion in heme is the Fe^{2+} ion around which four nitrogen atoms are coordinated that belong to a complex ligand with cyclic groups. Hemoglobin reversibly attaches oxygen and carries it from the lungs via the blood vessels to all the tissues. Chlorophyll, which participates in photosynthesis processes in plants, has a similar structure, but its central ion is Mg^{2+} .

All the classes of complex compounds listed above contain one central atom, i.e. they are **mononuclear**. Complexes are also encountered with a more complicated structure that contain two or more central atoms of the same or different elements. These complexes are known as **polynuclear** ones.

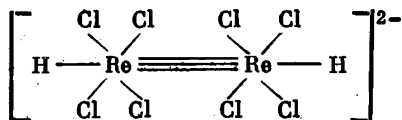
There are different kinds of polynuclear complexes.

Complexes with Bridge Atoms or Groups of Atoms. Examples are

complexes with bridge atoms of chlorine $\text{—}\ddot{\text{Cl}}\text{—}\rightarrow(\text{chloro-})$ and oxygen $\text{—}\ddot{\text{O}}\text{—}(\text{oxo-})$, and with the bridge group $\text{—}\ddot{\text{N}}\text{—}\rightarrow(\text{amino-})$ and

$\text{—}\ddot{\text{O}}\text{—}\rightarrow(\text{hydroxo-})$. For instance, the complex $[\text{Cr}(\text{NH}_3)_5\text{—OH}\rightarrow(\text{NH}_3)_5\text{Cr}]\text{Cl}_5$ is a binuclear complex with one bridge hydroxo-group. The dimer Al_2Cl_6 (see p. 305) also belongs to such compounds.

Cluster Complexes. Here the metal atoms are directly bonded to each other. This can be seen, for example, in the dimers $(\text{CO})_5\text{Mn—Mn}(\text{CO})_5$ and $[\text{Re}_2\text{H}_2\text{Cl}_8]^{2-}$. In the latter compound, there is a triple bond between the rhenium atoms:

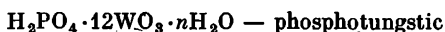
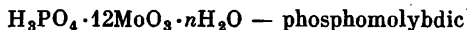


Polynuclear compounds also include isopoly and heteropoly acids.

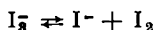
Isopoly acids are formed when two or more acid residues of the same oxyacid combine at the expense of oxygen bridges. They

include dichromic $\text{H}_2\text{Cr}_2\text{O}_7$, diphosphoric $\text{H}_4\text{P}_2\text{O}_7$, tetraboric $\text{H}_2\text{B}_4\text{O}_7$ acids, and also polysilicic acids forming the basis of silicates.

Heteropoly acids contain at least two different acids or oxides (derivatives of a non-metal and a metal) and a large amount of water (up to 30 molecules). The following heteropoly acids are the most important in analytical chemistry:



A few complexes are known in which the coordination centre is an anion. These are the **polyhalides** containing the anions $[\text{I} \cdot x\text{I}_2]^-$ (where x varies from 1 to 4) or $[\text{Br} \cdot x\text{Br}_2]^-$ (where x is 1 or 2). Mixed polyhalide anions also exist, namely, $[\text{I} \cdot \text{Br}_2]^-$ and $[\text{I} \cdot \text{Cl}_2]^-$. A major role in their formation is played by polarization: the greater the intensity of the polarization interaction between the anion E^- and the molecule E_2 , the more stable is the complex. This is exactly why polyiodides are the most stable of these compounds (the molecules I_2 readily polarize), while polyfluorides have not been obtained. (Owing to the equilibrium



in solution, a polyiodide solution exhibits properties of free iodine.

There are many ways of naming complex compounds, including the tradition of giving them the names of the investigators who discovered them. This way, although it pays a tribute of respect to scientists, makes memorizing of the names difficult. We give below the nomenclature of the principal kinds of complex compounds based on the recommendations of the International Union of Pure and Applied Chemistry.

The name of a complex anion begins with an indication of the composition of the inner sphere.

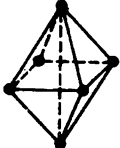
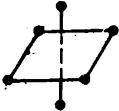
In the latter, first the anions are named, and their Latin names take an *-o* ending. Examples are Cl^- —**chloro**, CN^- —**cyano**, SO_3^{2-} —**sulphito**, and OH^- —**hydroxo**. Next the neutral ligands are named. The more common ones have common names such as **ammine** for coordinated ammonia, and **aqua** for water. The number of identical ligands is indicated by the Greek prefixes *mono-* for 1 (often omitted), *di-* (2), *tri-* (3), *tetra-* (4), *penta-* (5), and *hexa-* (6). After this, the central atom is named, with a Roman numeral in parentheses to indicate the oxidation state. The central atom takes an *-ate* ending,

and the Latin names are used for Fe, Cu, Sn, Pb, and Ag. The complex part is written all as a single word with the oxidation state as part of the word. Outer-sphere cations are named before the name of the complex, and outer-sphere anions after it. The oxidation state of the central atom is not indicated for non-electrolytes because it is determined uniquely from the electroneutrality of the complex. If the central atom is part of a cation, the trivial name of the element is used with its oxidation state in parentheses. Examples of naming complex compounds are given below:

$K_3[Fe(CN)_5NH_3]$ — potassium pentacyanoammineferrate(III)
 $(NH_4)_2[Pt(OH)_2Cl_4]$ — ammonium dihydroxotetrachloroplatinate(IV)
 $[Cr(H_2O)_3F_3]$ — trifluorotriaquachromium
 $[Co(NO_2)_2Cl(NH_3)_3]$ — dinitrochlorotriamminecobalt
 $[Pt(NH_3)_4Cl_2]Cl_2$ — dichlorotetrammineplatinum(IV) chloride
 $[Ag(NH_3)_2]Cl$ — diamminesilver(I) chloride

91. Spatial Structure and Isomerism

Identical ligands are symmetrically arranged in the space around the central atom. The even coordination numbers 2, 4, and 6 are encountered more often. The following geometrical configurations correspond to them:

Coordination number	Geometrical configuration	
2		—linear
		—square-planar
4		—tetrahedral
6		—octahedral, depicted schematically in the form:
		

The first correct notions on the spatial structure of complex compounds were formulated by A. Werner. He proceeded from the experimentally found number of isomers when there are two or more different ligands in a complex and compared it with the possible number for an assumed configuration. For instance, for the coordination number 4 and a tetrahedral configuration, all the positions of the ligands relative to the central atom are equivalent. Consequently, tetrahedral complexes of the $[MA_2B_2]$ type (where M is the central atom and A and B are ligands) have no isomers. Matters are different in complexes of platinum(II). For example, $[Pt(NH_3)_2Cl_2]$ is encountered in two isomeric forms differing in colour, solubility, dipole moment, reactivity, and the ways of preparation. This led to the conclusion that the ligands are arranged in a square about the central atom because it is exactly for this configuration that compounds of the $[MA_2B_2]$ type should have two isomers. In one of the isomers of the complex $[Pt(NH_3)_2Cl_2]$, the chlorine atoms are diagonally opposite (*trans*-isomer), and in the other one they are adjacent to each other (*cis*-isomer) (Fig. 52).

A growth in the number of different substituents is attended by an increase in the number of isomers, and for compounds of the $[MABCD]$ type with a square-planar configuration, already three isomers are possible.

In studying the isomerism of complex compounds with the coordination number 6, Werner arrived at the conclusion that in this case the ligands must be arranged symmetrically about the central ion, forming a regular octahedron (Fig. 53). If all the coordinated groups are identical, as shown in the figure, the interchanging of the groups will, naturally, fail to change the structure of the complex. But if the groups are different, they may be arranged differently, owing to which isomers can form. Indeed, experiments show that, for example, the compound $[Pt(NH_3)_2Cl_4]$ (where the coordination number of the platinum is 6) exists in two isomeric forms differing from each other in their colour and in other properties. The struc-

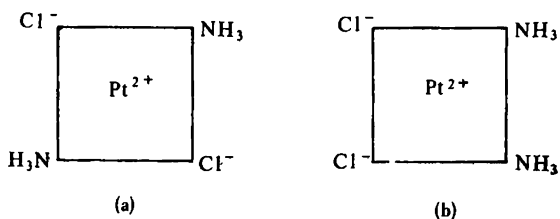
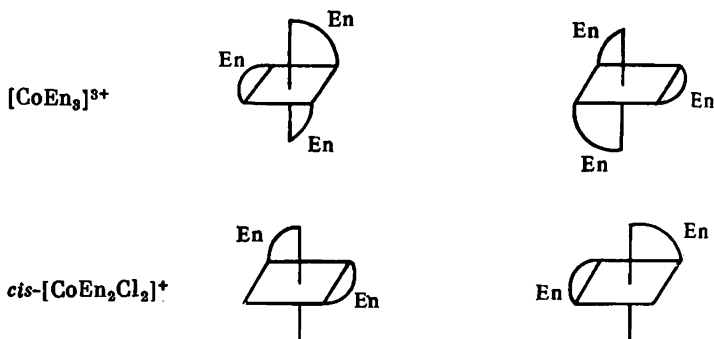


Fig. 52. Spatial structure of $[Pt(NH_3)_2Cl_2]$ isomers:
a—*trans*-isomer; b—*cis*-isomer

ture of these isomers according to Werner is shown schematically in Fig. 54. In one case, the NH_3 molecules are at diagonally opposite corners of the octahedron (*trans*-isomer), and in the other at adjacent corners (*cis*-isomer). Such spatial isomerism (known as **stereoisomerism**) is also observed in a number of other complexes with six ligands in the inner sphere.

Werner's assumptions on the octahedral structure of a complex having the coordination number 6 were brilliantly confirmed by the X-ray investigation of crystals of the relevant compounds. Figure 55 depicts the crystal lattice of the complex salt $\text{K}_2[\text{PtCl}_6]$. The complex ions $[\text{PtCl}_6]^{2-}$ in it are at the corners and centres of the faces of a cube, the chloride ions in the complex being arranged at the corners of a regular octahedron. Thus, the $[\text{PtCl}_6]^{2-}$ ion not only remains intact in solutions, but is also an independent structural unit in a crystal lattice.

Mirror (optical) isomerism considered on an earlier page (p. 132) using organic compounds as an example can also be related to geometrical isomerism. For instance, the complexes $[\text{CoEn}_3]\text{Cl}_3$ (En stands for ethylenediamine) and *cis*- $[\text{CoEn}_2\text{Cl}_2]\text{Cl}$ exist in the form of two mirror antipodes:



In addition to geometrical isomerism, other kinds of isomerism of complex compounds are known due to the different position and bonding of the ligands in the inner sphere. For instance, **hydrate** isomerism occurs when water passes from the inner sphere to the outer one, for example $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$, and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$. The colour of the complex changes from blue-violet in $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ to light green in $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (see also p. 326).

Ionization isomerism is determined by the different distribution of the ions between the inner and outer spheres, for instance $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$, $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$, $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$, and $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$.

Coordination isomerism is associated with the transition of ligands from one complexing agent to another: $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$.

There are also polymers among the complex compounds. For instance, the isomeric *cis*- and *trans*-monomers $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, the dimers $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$, $[\text{Pt}(\text{NH}_3)_3\text{Cl}][\text{Pt}(\text{NH}_3)\text{Cl}_3]$, and the trimer $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2 \cdot [\text{PtCl}_4]$ correspond to the composition $\text{PtCl}_2 \cdot 2\text{NH}_3$.

92. Nature of the Chemical Bond in Complex Compounds

The formation of many complex compounds can be explained in a first approximation by electrostatic attraction between the central metal cation and the anions or polar molecules of the ligands. Forces of electrostatic repulsion between identically charged (or, for polar molecules, identically oriented) ligands act in addition to the forces of attraction. As a result, the most stable grouping of the atoms (ions) is formed that has a minimum potential energy.

Quantitative calculations based on such an electrostatic model were first performed by W. Kossel and A. Magnus. They assumed ions to be undeformed spheres and took into account their interaction according to Coulomb's law. The results of these calculations show satisfactorily how the coordination number depends on the charge of the central ion. The simple electrostatic theory, however, is not capable of explaining the selectivity (specificity) of complexing because it takes no account of the nature of the central atom and ligands, and of the features of the structure of their electron shells. To take these factors into consideration, the electrostatic theory was supplemented with polarization notions (see Vol. 1, Sec. 46), according to which complexing is facilitated by the participation, as the central atoms, of small multiply charged cations of *d* elements having a strong polarizing action, and as the ligands, of large readily polarizing ions or molecules. In this case, deformation of the electron shells of the central atom and ligands occurs that leads to their mutual penetration. This is exactly what causes strengthening of the bonds.

The polarization ideas were useful for explaining the stability, acid-base, and oxidation-reduction properties of complex compounds, but many other of their properties remained unex-

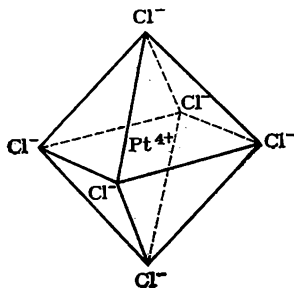


Fig. 53. Spatial structure of the complex ion $[\text{PtCl}_6]^{3-}$.

plained. For instance, from the angles of view of the electrostatic theory, all complexes with the coordination number 4 must have a tetrahedral structure because the smallest mutual repulsion of the ligands corresponds to this configuration. Actually, as we already know, some of such complexes, for example those formed by platinum(II), have a square-planar structure. The electrostatic theory cannot explain the features of the reactivity of complex compounds, their magnetic properties, and colour. A more accurate and complete description of the properties and structure of complex compounds can be obtained only on the basis of quantum-mechanical notions of the structure of atoms and molecules.

At present, there are several approaches to a quantum-mechanical description of the structure of complex compounds.

The crystal field theory (or ligand field theory) is based on the notion of the electrostatic nature of the interaction between a central ion and ligands. Unlike the simple ionic theory, however, here account is taken of the different spatial arrangement of the d orbitals (see Fig. 20 in Vol 1, p. 88) and the associated different change in the energy of the central atom's d electrons due to their repulsion from the electron clouds of the ligands.

Let us consider the state of central ion d orbitals. In a free ion, the electrons in each of the five d orbitals have the same energy (Fig. 56a). We shall assume that the ligands set up a uniform spherical electrostatic field with the central ion at its centre. In this hypothetical case, the energy of the d orbitals, at the expense of the repulsive action of the ligands, grows by the same value, i.e. all the d orbitals remain equivalent as regards their energy (Fig. 56b). Actually, however, the ligands act differently on different d orbitals: if an orbital is close to a ligand, the energy of the electron occupying it grows more considerably than when the orbital is farther from the ligand. For example, with an octahedral arrangement of the ligands about the central ion, the electrons in the orbit

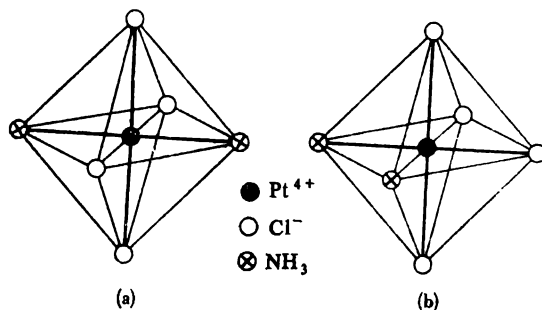


Fig. 54. Spatial structure of the isomers of $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]$:
a—trans-isomer; b—cis-isomer

als d_{z^2} and $d_{x^2-y^2}$ directed towards the ligands experience the greatest repulsion (Fig. 57a and b); therefore their energy will be higher than in a hypothetical spherical field. Conversely, the d_{xy} , d_{xz} , and d_{yz} orbitals are directed between the ligands (Fig. 57c) so that the energy of the electrons here will be lower than in a spherical field. Hence, the d level of the central ion splits into two energy levels in an octahedral field of ligands (Fig. 56c)—a higher level corresponding to the orbitals d_{z^2} and $d_{x^2-y^2}$ (they are customarily designated d_g or e_g) and a lower level corresponding to the orbitals d_{xy} , d_{xz} , and d_{yz} (these orbitals are designated d_e or t_{2g}).

The difference between the energies of the levels d_g and d_e known as the crystal-field splitting energy is designated by the symbol Δ . It can be determined experimentally according to the absorption spectra of the complex compounds. The value of Δ depends both on the nature of the central atom and on that of the ligands: ligands producing a strong field cause greater splitting of the energy levels, i.e. result in a higher value of Δ .

With respect to their splitting energy, ligands are arranged in the following sequence (the spectrochemical series*):



strong
field

moderate field

weak field

The ligands setting up the strongest field are at the beginning of the series, and those setting up a weak field are at its end.

The electrons of the central ion are distributed among the d orbitals so as to form a system with the minimum energy. This can be achieved in two ways: by location of the electrons on the d_e orbitals corresponding to a lower energy, or by their uniform distribution over all the d orbitals in accordance with Hund's rule (see Vol. 1, p. 95). If there are not more than three electrons in the d orbitals of the central ion, according to Hund's rule they are in the orbitals of the lower energy level d_e . For instance, in the Cr^{3+} ion having a $3d^3$ electron configuration of its outer layer, each of the three d electrons occupies one of the three d_e orbitals.

* The mutual arrangement of ligands with close splitting energies may change somewhat when going over to another central atom or even when the oxidation state of the central atom changes.

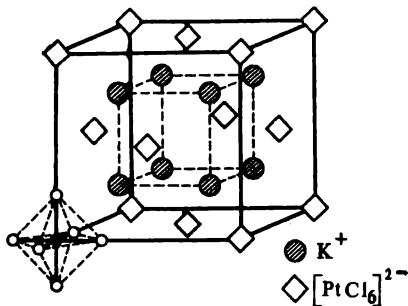


Fig. 55. Crystal lattice of $\text{K}_3[\text{PtCl}_6]$

Matters are different when there is a greater number of electrons on the d orbitals of the central ion. Their location in accordance with Hund's rule requires the expenditure of energy for transferring some electrons to d_y orbitals. On the other hand, when the maximum number of electrons are located in d_e orbitals, Hund's rule is violated and, consequently, energy must be spent for transferring some of the electrons to orbitals already having one electron each. Consequently, when the field is weak, i.e. the value of the splitting energy is low, it is more energetically advantageous for the d electrons to be uniformly distributed between all the d orbitals (in accordance with Hund's rule); the central ion retains a high value of its spin, so that a **high-spin** paramagnetic complex is formed. When the field is strong (a high value of the splitting energy), it is more energetically advantageous to accommodate the maximum number of electrons in d_e orbitals; here a **low-spin** diamagnetic complex is created.

From this standpoint, it is clear why, for example, the complex $[\text{CoF}_6]^{3-}$ is paramagnetic, and the complex $[\text{Co}(\text{CN})_6]^{3-}$ is diamagnetic. The position of the ligands F^- and CN^- in the spectrochemical series (see above) shows that a considerably higher splitting energy Δ corresponds to the CN^- ions than to the F^- ions. Therefore, in the complexes being considered, the electrons of the central Co^{3+} ion are distributed between the d orbitals as shown in Fig. 58: the complex $[\text{CoF}_6]^{3-}$ is a high-spin one, and the complex $[\text{Co}(\text{CN})_6]^{3-}$ is a low-spin one.

We have considered the crystal-field theory as applied to complexes with an octahedral arrangement (octahedral coordination) of the ligands. We could consider the properties of complexes with a different, for example tetrahedral, coordination from similar angles of view.

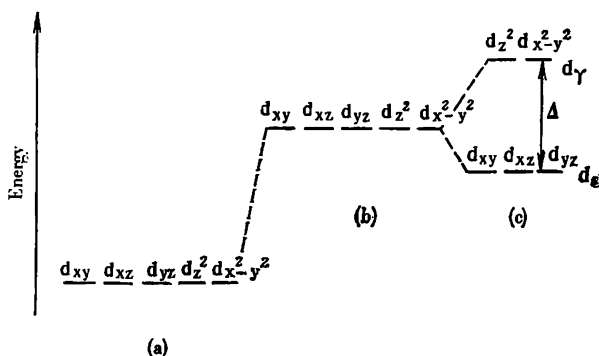


Fig. 56. Energy levels of central ion d orbitals:

a—free ion; b—ion in hypothetical spherical field; c—ion in octahedral field of ligands

The crystal field theory allows us to explain not only the magnetic properties of complex compounds, but also their specific colour. For instance, in the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex, the Ti^{3+} ion has one d electron (its electron configuration is d^1). In the ground (unexcited) state, this electron is in one of the d_e orbitals, but upon the expenditure of a certain energy ($\Delta = 238 \text{ kJ/mol}$) it can become excited and pass over to the d_v orbital. The wavelength of the light absorbed in this transition and corresponding to this energy is 500 nm. This is exactly what explains the violet colour of the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex. When considered in this way, it becomes clear why complexes formed by Cu^+ , Ag^+ , Zn^{2+} , and Cd^{2+} , as a rule, are colourless; these ions have the electron configuration d^{10} so that all the d orbitals are filled and the transition of electrons from the d_e to the d_v orbitals is impossible. The Cu^{2+} ion, however, forms coloured complexes: it has the electron configuration d^9 so that one of the d_e electrons when excited can pass over to the d_v orbital.

Although the crystal field theory was fruitful in interpreting the magnetic, optical, and some other properties of complex compounds, it was not able to explain the positions of ligands in the spectrochemical series, and also the very fact of formation of certain complexes, for instance the "sandwich" compounds—dibenzene-chromium $\text{Cr}(\text{C}_6\text{H}_6)_2$, ferrocene $\text{Fe}(\text{C}_5\text{H}_5)_2$, and their analogues. The matter is that the crystal field theory, while taking into consideration the influence of ligands on the central ion, does not take into account the participation of the ligand electrons in the formation of chemical bonds with the central ion. This is why the application of the crystal field theory is restricted chiefly to complex compounds with a mainly ionic nature of the bond between the central atom and the ligands.

The valence bond method as applied to complex compounds is based on the same notions as in simple compounds (see Vol. 1, Secs. 39-44). It is taken into account that the chemical bonds appearing in complexing have a donor-acceptor origin, i.e. are formed at

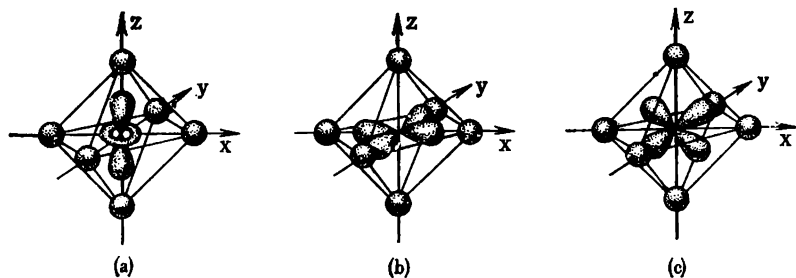
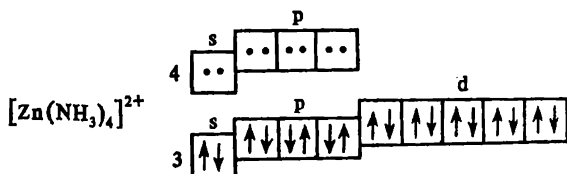


Fig. 57. Orbitals d_{z^2} (a), $d_{x^2-y^2}$ (b), and d_{xz} (c) in an octahedral field of ligands (the ligands are conditionally depicted as spheres)

the expense of an unshared electron pair of one of the interacting atoms and the free orbital of the other atom. Let us consider the structure of certain complex compounds from these standpoints.

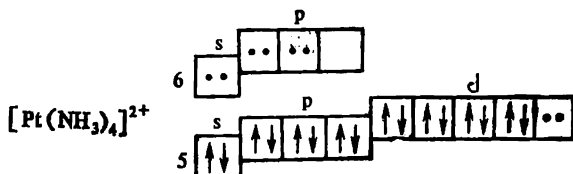
In an ammonia molecule, the nitrogen atom is in a state of sp^3 hybridization, and there is an unshared electron pair on one of its hybrid orbitals. Therefore, upon the donor-acceptor interaction of an NH_3 molecule with an H^+ ion, the NH_4^+ ion is formed that has a tetrahedral configuration. The complex $[\text{BF}_4]^-$ ion has a similar structure: here the donor of the electron pair is the anion F^- , while the acceptor is the boron atom in the BF_3 molecule having an unfilled orbital in its outer electron layer and passing over to the state of sp^3 hybridization in complexing.

Certain complexes of elements of the zinc subgroup have the same geometrical configuration (a tetrahedron). Examples are $[\text{Zn}(\text{NH}_3)_4]^{2+}$, $[\text{Cd}(\text{NH}_3)_4]^{2+}$, and $[\text{HgI}_4]^{2-}$. For instance, in $[\text{Zn}(\text{NH}_3)_4]^{2+}$, the zinc ion accommodates the electron pairs of the ligands (conditionally depicted by dots in the diagram) on one $4s$ and three $4p$ orbitals.



Here sp^3 hybridization occurs that corresponds to the location of the ligands at the corners of a tetrahedron (tetrahedral coordination).

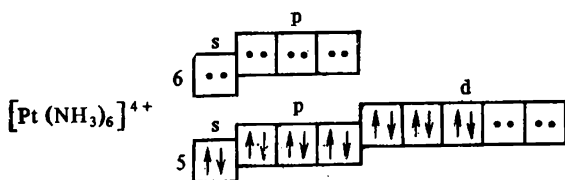
The ions of d elements with four occupied d orbitals (Pt^{2+} , Pd^{2+} , and Au^{3+}) with the coordination number 4 accommodate the electron pairs of the ligands on one $(n-1)d$, one ns and two np orbitals. For example, in $[\text{Pt}(\text{NH}_3)_4]^{2+}$, we have:



Here dsp^2 hybridization occurs that corresponds to location of the ligands at the corners of a square (square coordination). For this reason, complexes such as $[\text{Pt}(\text{NH}_3)_4]^{2+}$ and $[\text{PtCl}_4]^{2-}$ have a square-planar structure.

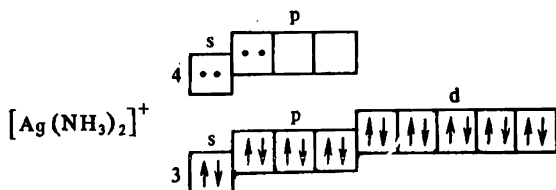
The hybridization d^2sp^3 and an octahedral arrangement of the ligands correspond to the coordination number 6. Such coordina-

tion occurs, for example, in platinum(IV) complexes:



Similar octahedral coordination occurs in such complexes as $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{4-}$, and $[\text{RhCl}_6]^{3-}$.

Hybridization of the sp type and linear coordination of the ligands correspond to the coordination number 2. For example, in $[\text{Ag}(\text{NH}_3)_2]^+$, we have:



The above examples show that the valence bond method successfully explains definite values of the coordination numbers and the geometrical shapes of the complex particles, as well as the differences in magnetic properties (diamagnetism or paramagnetism) of complex compounds. Some of their properties, however (for instance, the absorption spectra) are not explained satisfactorily by this method. In addition, the interaction between the central atom and the ligands in complex compounds does not only consist in the

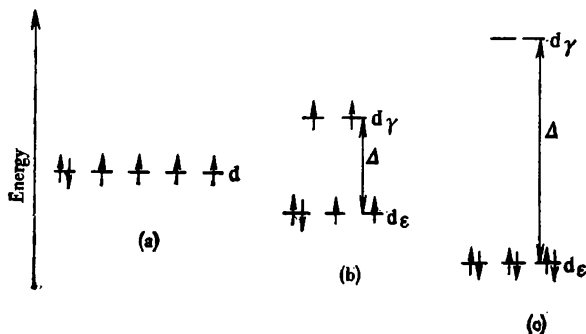


Fig. 58. Distribution of electrons of Co^{2+} ion between d orbitals:

a—in hypothetic spherical field; *b*—in weak octahedral field of ligands (complex $[\text{CoF}_6]^{3-}$); *c*—in strong octahedral field of ligands (complex $[\text{Co}(\text{CN})_6]^{3-}$)

transfer of electrons from the ligand. There are ligands that can receive metal electrons in vacant orbitals, for instance in free d orbitals (in the PF_3 molecule or the SnCl_3^- ion), or in unfilled anti-bonding orbitals (in C_2H_4 , CO , and NO molecules). Such ligands are called π acceptors, and their bond with the central atom a π -dative one. The structure of many of the complex compounds discovered lately, for instance of the "sandwiches" (see above), cannot be explained from the angle of view of the valence bond method.

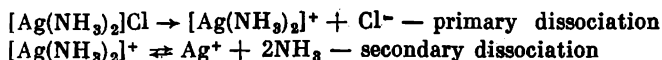
The Molecular Orbital Method. Molecular orbitals are formed in complex compounds according to the same principle and have the same properties as the molecular orbitals in diatomic molecules (see Vol. 1, Sec. 45). A distinction is that in complex compounds the molecular orbitals are multiple-centre delocalized ones, as is the case, for instance, in the benzene molecule (see Sec. 53).

The MO method has at present become the leading, most fruitful one in the theory of complex compound structure. Particularly, it successfully explains the structure and properties of the above-mentioned "sandwich" compounds such as $\text{Cr}(\text{C}_6\text{H}_6)_2$ and $\text{Fe}(\text{C}_5\text{H}_5)_2$ in which the central atom is between cyclic organic molecules and is bonded to them by means of delocalized multiple-centre bonds. The application of the MO method to the explanation of the structure of complex compounds is treated in special books on the subject.

93. Stability of Complex Compounds in Solutions

We have already mentioned that the inner and outer spheres of complex compounds differ greatly in their stability. The particles in the outer sphere are bonded to the complex ion mainly by electrostatic forces and are readily detached in an aqueous solution.

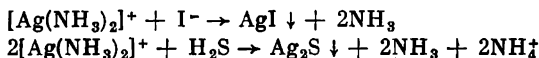
This dissociation is called **primary**. It proceeds almost to the end like the dissociation of strong electrolytes. The ligands in the inner sphere are much more strongly bonded to the central atom and are detached only to a small degree. The reversible decomposition of the inner sphere of a complex compound is known as **secondary dissociation**. For example, the dissociation of the complex $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ can be written as follows:



Secondary dissociation is characterized by the existence of equilibrium between the complex particle, the central ion, and the ligands. The correctness of this statement can be seen from the following reactions. If a solution containing the complex ion $[\text{Ag}(\text{NH}_3)_2]^+$ is reacted with a solution of a chloride, no precipitate

is formed, although a silver chloride precipitate separates from solutions of ordinary silver salts when chlorides are added to them. The concentration of the silver ions in the ammonia solution is evidently too small to ensure the value of the solubility product of silver chloride [$K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$] to be reached even when an excess amount of chloride ions is introduced into it. But after the addition of potassium iodide to the solution of the complex, a silver iodide precipitate separates. This proves that there nevertheless are silver ions in the solution. No matter how small their concentration is, it is sufficient for the formation of a precipitate because the solubility product of silver iodide AgI is only 1×10^{-16} , i.e. is much smaller than that of silver chloride. In exactly the same way, a reaction with hydrogen sulphide yields a precipitate of silver sulphide Ag_2S whose solubility product is 10^{-51} .

The equation of the proceeding reactions can be written as follows:

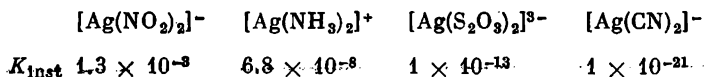


The dissociation of the $[\text{Ag}(\text{NH}_3)_2]^+$ ions in accordance with the above equation, like the dissociation of any weak electrolyte, obeys the law of mass action and can be characterized by the relevant equilibrium constant, known as the constant of instability of the complex ion:

$$K_{\text{inst}} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[[\text{Ag}(\text{NH}_3)_2]^+]} = 6.8 \times 10^{-8}$$

The instability constants for various complex ions are quite diverse and can be a measure of the stability of a complex. The instability constants whose expression includes the concentrations of ions and molecules are called "concentration" ones. The instability constants containing the activities of ions and molecules instead of their concentrations are more accurate and do not depend on the concentrations and ionic strength of a solution. These two different expressions for the instability constants coincide with each other for dilute solutions.

A glance at the above formula shows that the *smaller* the concentration of the decomposition products, i.e. the *more stable* is a complex, the *smaller* is its instability constant. The complex particles that are the most stable in solutions have the lowest instability constants. For instance, among the following compounds of the same kind:



the stability of the complex grows in going from $[\text{Ag}(\text{NO}_2)_2]^-$ to $[\text{Ag}(\text{CN})_2]^-$. The ion $[\text{Ag}(\text{CN})_2]^-$ is so stable that even the addition

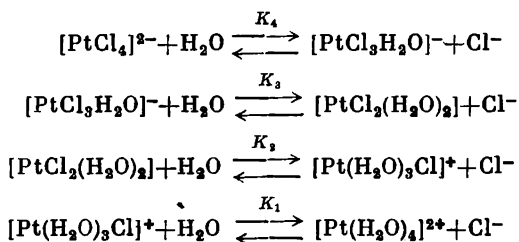
of potassium iodide to a solution of the complex salt does not lead to the formation of a silver iodide precipitate. But when reacted with hydrogen sulphide, owing to the negligibly small value of the solubility product of silver sulphide, a precipitate of silver sulphide is nevertheless formed.

Lately, it is preferable practice to use the reciprocal of the instability constant, called the **stability constant**, to characterize the stability of complex compounds. For the $[\text{Ag}(\text{NH}_3)_2]^+$ ion, the stability constant is:

$$K_{\text{stab}} = \frac{1}{K_{\text{inst}}} = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

Up to now, we dealt with the *overall* constants of instability and stability relating to the decomposition of a complex into its final products. What actually occurs in solutions is *stepped* dissociation of a complex similar to the stepped dissociation of weak electrolytes, for instance of polybasic acids.

For example, an aqueous solution of $\text{K}_2[\text{PtCl}_4]$ contains in different proportions all the complexes participating in the following equilibria:



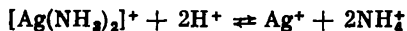
Each of these equilibria is characterized by its own step constant of instability K_4 , K_3 , etc. As the chloride ions detach, the charge of the complex becomes more and more positive, while the number of Cl^- ions in the complex diminishes. As a result, the consecutive detachment of the chloride ions becomes more and more difficult. For this reason, the relationship $K_4 > K_3 > K_2 > K_1$ holds between the step instability constants of the $[\text{PtCl}_4]^{2-}$ ion.

Such a change in the values of the consecutive instability constants bears a general nature.* The magnitude of the overall instability constant equals the product of all the step constants.

The values of the instability and stability constants are given in chemical reference books. These quantities can be used to predict the course of reactions between complex compounds: with a great difference in the stability constants, a reaction will proceed in the

* There is a small number of deviations caused by disproportionation or by the action of additional factors leading to the preferable stabilization of one of the equilibrium forms.

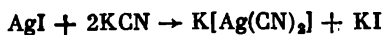
direction of the formation of a complex with a greater stability constant or, which is the same, with a smaller instability constant. For example, for the $[\text{Ag}(\text{NH}_3)_2]^+$ ion, $K_{\text{inst}} = 6.8 \times 10^{-8}$, and for the NH_4^+ ion, $K_{\text{inst}} = 5.4 \times 10^{-1}$. Consequently, reaction with acids decomposes amminesilver with the formation of Ag^+ and NH_4^+ ions:



The complex $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ($K_{\text{inst}} = 5 \times 10^{-34}$) does not decompose at room temperature even in concentrated hydrochloric acid.

Complexing is widely used in analytical chemistry. The conditions for the most effective separation of ions are chosen with a view to the ratio of the stability constants for the complex compounds they form.

For instance, the cations Ni^{2+} , Co^{2+} , and Zn^{2+} produce stable soluble amines, whereas Al^{3+} , Fe^{3+} , and Cr^{3+} are less inclined to form complexes with ammonia and precipitate in the form of hydroxides when reacted with ammonia. This allows these two groups of cations to be separated by the action of ammonia. Similar considerations can be used for separating anions: for instance, a mixture of chlorides and iodides can be precipitated as AgCl and AgI and then treated with ammonia—only AgCl will pass into the solution. To dissolve the AgI , a ligand must be used that binds the Ag^+ ion considerably more strongly, for instance, CN^- , because for the $[\text{Ag}(\text{CN})_2]^-$ complex we have $K_{\text{inst}} = 1 \times 10^{-21}$. Silver iodide dissolves in a solution of KCN to form $\text{K}[\text{Ag}(\text{CN})_2]$:

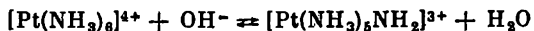


The stability constants of complexes of the same kind depend on a number of factors and first of all on the nature of the central atom and the ligands. In complexes with central ions having a weak polarizing power, for example with ions of the alkali and alkaline-earth metals, the stability grows with an increase in the intensity of the electrostatic interaction between the central ion and the ligands: the stability of complexes grows with an increase in the charges of the central ion and ligands and with a decrease in their radii. These cations form more stable complexes with ligands containing elements of small periods (oxygen, nitrogen) and with F^- ions.

For another large group of complexing agents—cations of the platinum metals and the ions Hg^{2+} , Ag^+ , and Au^{3+} having a strong polarizing power and for which the nature of bonding between the central atom and the ligands approaches a covalent one—complexes with readily polarizing ligands are the most stable. The latter include I^- ions and ligands containing P and S atoms.

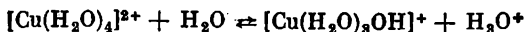
94. Influence of Coordination on the Properties of Ligands and the Central Atom. Mutual Influence of Ligands

Coordination is associated with a change in the electron configuration of ligands and as a result leads to a change in their properties. This can be seen quite well on the example of the acid and basic properties of complex compounds. Whereas free ammonia has basic properties in an aqueous solution, the $[\text{Pt}(\text{NH}_3)_6]^{4+}$ complex exhibits the properties of an acid and enters into a reversible reaction with an alkali:



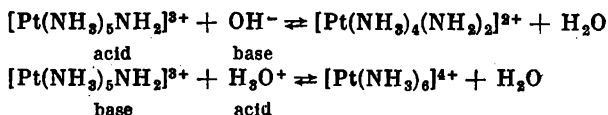
The reason for the change in the properties of ammonia is that its coordination is attended by shifting of the electron density towards the positively charged central atom. As a result, the effective negative charge of the nitrogen atom in the NH_3 molecule sharply diminishes, and this facilitates detachment of a proton.

Other polar or readily polarizing molecules capable of displaying proton-donor properties such as H_2O , NH_2OH , and organic amines behave similarly in a field of cations of some of the transition metals. Playing the role of ligands, these molecules are capable of detaching a proton in aqueous solutions and from the point of view of the proton theory of acids and bases (Vol. 1, p. 258) behave like acids. For example, the reaction of a hydrated copper ion with water should be written as follows:



This equation expresses the process of hydrolysis of a copper ion. Hence, the hydrolysis of cations in aqueous solutions can be considered as the acid dissociation of the water in aquacomplexes.

If a complex compound simultaneously contains a proton-donor molecule of a ligand (for instance, H_2O or NH_3) and a molecule of the same ligand that has detached a proton and is therefore capable of attaching it (for example, OH^- or NH_2^-), it is amphoteric. For instance, $[\text{Pt}(\text{NH}_3)_5\text{NH}_2]^{3+}$ in a reaction with an alkali behaves like an acid, and in a reaction with an acid like a base:



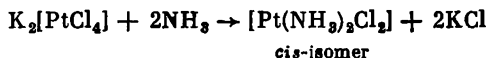
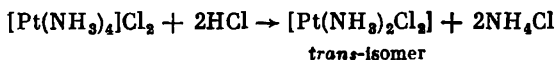
A compound containing only deprotonized ions (OH^- , NH_2^- , NH_2O^- , etc.) always behaves like a base.

The fundamentals of the theory of acid and basic properties of complex compounds were developed by A. Grinberg*.

A central ion also changes its properties as a result of complexing, which can be seen, for example, by the change in the relevant electrode potential. The standard electrode potential φ° of the system $\text{Fe}^{3+}/\text{Fe}^{2+}$ in an aqueous solution, for instance, is +0.771 V. If we take cyanide complexes containing iron in the oxidation state +2 and +3, for the system $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ we have $\varphi^\circ = +0.36$ V, whence it follows that this system has weaker oxidizing properties than the system $\text{Fe}^{2+}/\text{Fe}^{3+}$. In the given most typical case, the transition from hydrated ions to the more stable complexes is attended by the stabilization mainly of the complex ion containing the central atom in the higher oxidation state, as a result of which the oxidizing power of this ion decreases.

In addition to the influence of complexing on the properties of the ligands and central atom, there is also mutual influence of the ligands in the complexes. Its most striking manifestation is *trans*-influence discovered by I. Chernyaev**. The essence of this phenomenon consists in that in complexes in which *cis*- and *trans*-isomers are possible, the mutual influence of the ligands is observed (the most strongly when they are in the *trans*-position relative to each other).

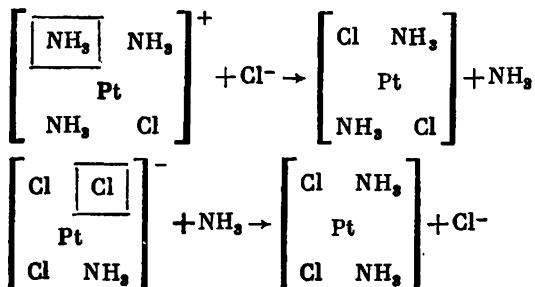
Some ligands (they are called *trans*-active) weaken the action of the central atom on the properties of a ligand in the *trans*-position with respect to the ligand being considered and cause them to approach the properties of a free ligand. An example of the manifestation of *trans*-influence is the preparation of isomers of diammineplatinum(II). When a tetrammineplatinum(II) complex is heated with concentrated HCl, a *trans*-isomer is generally obtained, while when ammonia is reacted with $\text{K}_2[\text{PtCl}_4]$, a *cis*-isomer is obtained:



* Aleksandr Abramovich Grinberg (1898-1966) was an eminent Soviet inorganic chemist, an academician, and State Prize winner. The main works by A. Grinberg are devoted to a study of the spatial structure, acid and basic, and oxidation-reduction properties of complex compounds. He made a number of valuable generalizations on how coordination affects the properties of the central atom and ligands, and on the reactivity of complex compounds.

** Ilya Ilyich Chernyaev (1893-1966), a prominent Soviet inorganic chemist, an academician, and State Prize winner, was a pupil of L. Chugaev. His main interests were in the field of the chemistry of complex compounds, chiefly platinum and the platinum metals. In 1926, he discovered the phenomenon of *trans*-influence, which made it possible to carry out the directed synthesis of a considerable number of complex compounds. I. Chernyaev was one of the organizers of the industry of platinum and the platinum metals in the USSR.

The explanation is the greater *trans*-influence of the Cl^- ion in comparison with the NH_3 molecule, and this is what determines the most labile ligand (enclosed in a dotted square) in the immediately formed complexes:



The kinetic characteristics of replacement reactions can also be used to assess the *trans*-influence of ligands. With respect to their ability of accelerating a replacement process of a *trans*-arranged ligand, the following ligand series can be formed: CN^- , C_2H_4 , $\text{CO} > \text{NO}_2^-$, I^- , $\text{SCN}^- > \text{Br}^- > \text{Cl}^- > \text{OH}^- > \text{NH}_3 > \text{H}_2\text{O}$.

Trans-influence has been established chiefly when studying the complexes of Pt(II) , but it also manifests itself in complexes with the central ions Pt(IV) , Co(III) , Au(III) , Pd(II) , and Rh(I) . *Trans*-influence is an electron effect and is associated with a change in the electron density. One of the first and most illustrative attempts to explain it was made on the basis of polarization notions: ligands with a greater *trans*-influence have a readily deformed electron shell and are good reducing agents (A. Grinberg and B. Nekrasov). It was later found that account must also be taken of the ability of a ligand to take part in π -acceptor interaction with the central atom.

Grinberg and his school discovered that in addition to *trans*-influence, there is also *cis*-influence of ligands (although in a weaker form). The change in the properties of the central atom and ligands in complexing, and also the existence of *trans*- and *cis*-influence of ligands are in complete accordance with Butlerov's theory of chemical structure that takes into consideration all the kinds of mutual influence of atoms and groups of atoms in molecules (see Vol. 1, Sec. 38 and Vol. 2, Sec. 48).

SECOND GROUP OF THE PERIODIC TABLE

MAIN SUBGROUP

The main subgroup of Group II includes the elements beryllium, magnesium, calcium, strontium, barium, and radium. All these elements except for beryllium have pronounced metallic properties. In the free state, they are grayish-white substances harder than the alkali metals and with rather high melting points. As regards their density, all of them except radium relate to the light-weight metals. Their most important properties are given in Table 10.

Table 10

Selected Properties of Beryllium, Magnesium, Radium
and the Alkaline Earth Metals

	Be	Mg	Ca	Sr	Ba	Ra
Configuration of outer electron layer of atom	$2s^2$	$3s^2$	$4s^2$	$5s^2$	$6s^2$	$7s^2$
Atomic radius, nm	0.113	0.160	0.197	0.215	0.221	0.235
Ionization energy of atom						
$E \rightarrow E^+, \text{ eV}$	9.32	7.65	6.11	5.69	5.21	5.28
$E^+ \rightarrow E^{2+}, \text{ eV}$	18.21	15.03	11.87	11.03	10.00	10.15
Radius of ion E^{2+} , nm	0.034	0.074	0.104	0.120	0.138	0.144
Standard enthalpy of atomization of metal at 25 °C, kJ per mole of atoms	320.5	150.2	192.5	164.0	175.7	130
Density, g/cm ³	1.85	1.74	1.54	2.63	3.76	About 6
Melting point, °C	1285	651	850	770	710	960
Boiling point, °C	2970	1107	1480	1380	About 1640	1140
Standard electrode potential of process $E^{2+} + 2e^- = E$, V	-1.847	-2.363	-2.866	-2.888	-2.905	About -2.92

The first two members of the subgroup being considered occupy a somewhat special position in it, differing in many respects from the other four elements. Beryllium in some of its properties approaches aluminium ("diagonal similarity"—see p. 280).

All the isotopes of the last element of the subgroup—radium—are radioactive. The long-lived isotope ^{226}Ra was previously used in radiotherapy; at present it has been replaced with cheaper isotopes of other elements formed in nuclear reactors.

The outer electron layer of the atoms of elements of this subgroup have two electrons, while in the preceding layer beryllium has two electrons, and the other elements eight. The atoms comparatively readily part with the two electrons of their outer layer and transform into positive doubly charged ions. Consequently, as regards their chemical activity, these elements are only slightly inferior to the alkali metals. Like the latter, they oxidize in the air quite rapidly and can displace hydrogen from water at room temperature. Beryllium and magnesium react with water very slowly, however, because the hydroxides formed are poorly soluble in water: they coat the surface of the metal and hinder the further course of the reaction. The other four metals, owing to the better solubility of their hydroxides, react with water much more vigorously.

The elements calcium, strontium, and barium in the main subgroup were named **alkaline earth metals** a long time ago. The origin of this name is associated with the fact that calcium, strontium, and barium hydroxides, like sodium and potassium hydroxides, have alkaline properties, while the oxides of these metals with respect to their refractoriness are similar to the oxides of aluminium and the heavy metals, which previously had the common name of **earths**.

Oxides are always obtained when alkaline earth metals are burned. The peroxides, if they in general form, are much less stable than their alkali metal counterparts.

The oxides of calcium, strontium, and barium combine directly with water to form hydroxides. The solubility of the latter greatly increases when going from calcium to the following alkaline earth metals. The basic properties of the hydroxides grow in the same sequence.

The alkaline earth metals can combine with hydrogen to form hydrides similar to the hydrides of the alkali metals (for instance, CaH_2).

The alkaline earth metals have the remarkable inclination of combining with nitrogen that grows with an increase in their atomic mass. Even at room temperature, the alkaline earth metals slowly combine with nitrogen to form nitrides.

Unlike the salts of the alkali metals, many salts of the alkaline earth metals are only sparingly soluble in water. These salts include the carbonates, sulphates, and phosphates.

The alkaline earth metals have an oxidation state of +2 in all their compounds.

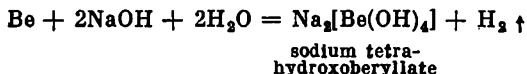
95. Beryllium

The amount of beryllium in the Earth's crust is quite meager [0.0004% (mass)]. It is contained in some minerals, the most frequently occurring one of which is beryl $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$. Some varieties of beryl coloured by impurities in different colours relate to precious stones. Among them are green emeralds and bluish-green aquamarines.

Metallic beryllium is prepared by electrolysis of melts of its compounds, chiefly beryllium chloride. The electrolyte is a melt containing 50% (mass) of BeCl_2 and 50% (mass) of NaCl . Such a composition allows the temperature at which electrolysis is conducted to be lowered to 300 °C (pure beryllium chloride melts at 440 °C).

Beryllium is a very hard, brittle, white, light-weight metal. It resists corrosion owing to the formation of an oxide film having protective properties on its surface. Water does not virtually react with beryllium, while in acids it dissolves quite readily with the liberation of hydrogen.

A feature of beryllium is that it also dissolves in aqueous solutions of alkalis to form hydroxoberyllates:



Metallic beryllium has many remarkable properties. Thin sheets of beryllium are good transmitters of X-rays and are an indispensable material for making the windows of X-ray tubes through which the rays emerge. But beryllium finds its main application in alloys, into which this metal is introduced to improve their properties. Besides beryllium bronzes (see p. 241), alloys of nickel with two to four per cent of beryllium are used whose resistance to corrosion, strength, and elasticity are comparable with high-quality stainless steels, and in some respects are superior to them. They are used to manufacture springs and surgical instruments. Small additions of beryllium to magnesium alloys improve their resistance to corrosion. Such alloys, and also alloys of aluminium with beryllium, are used in aircraft engineering. Beryllium is one of the best moderators and reflectors of neutrons in high-temperature nuclear reactors. In view of the valuable properties of beryllium, its production is rapidly growing.

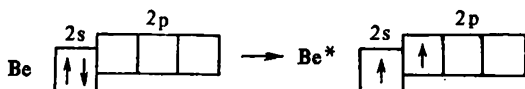
We have already indicated that the next-to-last electron layer in the beryllium atom has a different configuration than in the other elements of the subgroup: it contains only two electrons instead of eight. Consequently, in comparison with the other ele-

ments of the subgroup (see Table 10), the radius of the beryllium atom, and especially of its ion, is small out of proportion, its ionization energy is high, and its crystal lattice is very stable (a high melting point and a great enthalpy of atomization).

The difference between the configuration of the beryllium atom and that of the atoms of magnesium and the alkaline earth elements also tells on the properties of its compounds. For instance, $\text{Be}(\text{OH})_2$ is the only base in the subgroup having amphoteric properties (see below). Besides, the formation of ionic compounds is characteristic of the alkaline earth metals and magnesium, whereas beryllium atoms are usually bonded to atoms of other elements rather by a covalent bond than an ionic one.

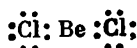
The chemical properties of beryllium are to a considerable extent similar to those of aluminium, which is in the third period and Group III of the periodic table, i.e. to the right of and lower than beryllium. This phenomenon, called *diagonal similarity*, is observed not only in beryllium, but also in some other elements. For example, many chemical properties of boron are similar to those of silicon.

In the formation of compounds of the BeX_2 type, for instance BeCl_2 , the beryllium atoms become excited:



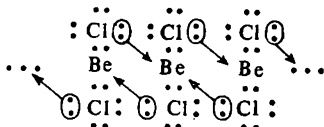
As a result of unpairing of the electrons, two covalent bonds are formed, and *sp* hybridization occurs: the valence electrons form two equivalent *sp* hybrid clouds extended in opposite directions. Hence, the BeX_2 molecules have a linear structure. The *sp* hybridization of the orbitals in a beryllium atom is treated in greater detail in Vol. 1, Sec. 43; see also Fig. 39 in Vol. 1.

The total number of valence electrons in molecules like BeCl_2 is not sufficient to completely fill the outer electron layer of the beryllium atom. This is why such molecules are called *electron-deficient*. For instance, in the BeCl_2 molecule



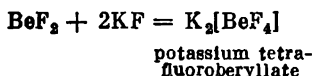
the outer layer of the beryllium atom contains only four electrons. This is why the beryllium atom can be an acceptor of electron pairs and form two more donor-acceptor covalent bonds. At the same time, each chlorine atom in the BeCl_2 molecule has unshared electron pairs and can play the role of their donor. Hence, when gaseous beryllium chloride is cooled, new covalent bonds appear between

individual BeCl_2 molecules as shown below:



The result is that when the beryllium chloride condenses, linear polymer chains are formed in which the chlorine atoms play the role of bridges bonding the beryllium atoms. Atoms performing such a function are known as **bridge atoms**. The structure of the linear polymer BeCl_2 is shown schematically in Fig. 59. Examination of the figure shows that the covalence and the coordination number of beryllium in solid BeCl_2 equal four.

This value of the covalence and the coordination number is typical of many stable beryllium compounds. For instance, when BeF_2 reacts with alkali metal fluorides, complex **fluoroberyllates** are formed containing the BeF_4^{2-} ion, for example:



Here the beryllium atom is in the state of sp^3 hybridization owing to which the BeF_4^{2-} ion has a tetrahedral structure. A tetrahedral arrangement of the beryllium and oxygen atoms is also characteristic of crystalline beryllium oxide. In aqueous solutions, the beryllium ion is apparently also in the form of tetrahedral aquacomplexes $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$.

Beryllium oxide BeO is a white, very refractory substance. It is used as a chemically stable refractory material (in jet engines, for manufacturing crucibles, in electrical engineering) and as a structural material in nuclear reactors.

Beryllium hydroxide $\text{Be}(\text{OH})_2$ has a pronounced amphoteric nature, which distinguishes it sharply from the hydroxides of the alkaline earth metals. It is practically insoluble in water, but dissolves readily both in acids and alkalis, in the latter case with the formation of hydroxoberyllates:

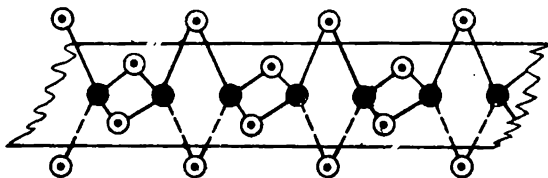


Fig. 59. Structure of the linear polymer $(\text{BeCl}_2)_n$: the black circles depict beryllium atoms, the white ones—chlorine atoms

The acid properties of beryllium hydroxide are very weak, and for this reason beryllates become greatly hydrolyzed in an aqueous solution.

Most beryllium salts, including the sulphate, dissolve well in water, whereas the sulphates of the alkaline earth metals are virtually insoluble in water. In aqueous solutions, the Be^{2+} ions become hydrolyzed, which is why solutions of beryllium salts have an acid reaction.

All beryllium compounds are toxic. Particularly, it is very dangerous to be in an atmosphere containing dust of beryllium or its compounds.

96. Magnesium

Magnesium is quite widespread in nature. It occurs in large amounts as magnesium carbonate forming the minerals magnesite MgCO_3 and dolomite $\text{MgCO}_3 \cdot \text{CaCO}_3$. Magnesium sulphate and chloride are contained in the potassium minerals kainite $\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ and carnallite $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The Mg^{2+} ion is contained in sea water, imparting a bitter taste to it. The total amount of magnesium in the Earth's crust is about 2% (mass).

Magnesium is produced chiefly by the electrolysis of molten magnesium chloride or dehydrated carnallite.

Magnesium is a silvery, very light-weight metal. It changes little in air because it rapidly becomes coated with a thin oxide film protecting it from further oxidation.

Although magnesium is far ahead of hydrogen in the electromotive series, it decomposes water very slowly, as we have already noted, because of the formation of the sparingly soluble magnesium hydroxide. Magnesium readily dissolves in acids with the liberation of hydrogen. Alkalies do not react with magnesium. When heated in air, magnesium burns to form magnesium oxide MgO and a small amount of magnesium nitride Mg_3N_2 .

The main field of application of metallic magnesium is the production of a variety of light-weight alloys based on it. The addition of small amounts of other metals to magnesium sharply changes its mechanical properties, imparting a considerable hardness, strength, and resistance to corrosion to the alloy. Alloys known as Elektron have especially valuable properties. They belong to three systems: Mg-Al-Zn , Mg-Mn , and Mg-Zn-Zr . Alloys of the first system containing from 3 to 10% Al and from 0.2 to 3% Zn have found the greatest use. A merit of magnesium alloys is their low density (about 1.8 g/cm^3). They are used first of all in rocket and aircraft engineering, and also in the motor vehicle industry and in instrument making. A shortcoming of magnesium alloys is their low

resistance to corrosion in a humid atmosphere and in water, especially sea water.

Pure magnesium is used in metallurgy. Some metals, particularly titanium, are produced by the magnesium-thermal method. In the production of certain steels and non-ferrous metal alloys, magnesium is used to remove oxygen and sulphur from them. Magnesium finds great application in organic synthesis. It is used to prepare a multitude of substances belonging to various classes of organic compounds, and also organo-element compounds. Mixtures of a magnesium powder with oxidizing agents are employed in the manufacture of flares and incendiary rockets.

Magnesium oxide MgO is usually prepared by roasting natural magnesite MgCO_3 . It is a white fluffy powder known more commonly as **magnesia usta**. Its high melting point (about 3000°C) allows its application in manufacturing refractory crucibles, pipes, and bricks.

Magnesium hydroxide $\text{Mg}(\text{OH})_2$ is obtained as a sparingly soluble white precipitate when alkalis are reacted with soluble magnesium salts. Unlike beryllium hydroxide, magnesium hydroxide has only basic properties, being a base of moderate strength.

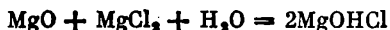
Magnesium sulphate $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, or **Epsom salt**, is contained in sea water. Unlike the sulphates of the alkaline earth metals, it dissolves well in water.

Magnesium chloride $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ forms colourless well soluble crystals deliquescent in air. The hygroscopicity of unpurified table salt is due to its containing small amounts of magnesium chloride.

Magnesium carbonate MgCO_3 is encountered in nature as the mineral magnesite.

When soda reacts with soluble magnesium salts, a mixture of basic carbonates is obtained instead of the neutral salt. This mixture is used in medicine under the name of **magnesia alba**.

Magnesium chloride hydroxide MgOHCl is of great industrial significance. The technical product is prepared by mixing magnesium oxide with a concentrated aqueous solution of magnesium chloride and is called **magnesia cement**. Such a mixture hardens after a certain time elapses and transforms into a compact white, readily polishable body. The hardening can be explained by the fact that the basic salt initially formed according to the equation



then polymerizes into chains of the kind $-\text{Mg}-\text{O}-\text{Mg}-\text{O}-\text{Mg}-$ whose ends accommodate chlorine atoms or hydroxyl groups.

Magnesia cement is used as a binder in the manufacture of millstones, whetstones, and various slabs. A mixture of it with sawdust named **Xylolite** is used as flooring.

The natural magnesium silicates—**talcum** $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ and especially **asbestos** $\text{CaO} \cdot 3\text{MgO} \cdot 4\text{SiO}_2$ find great application. Asbes-

tos, owing to its refractoriness, low thermal conductivity, and fibrous structure, is an excellent thermal-insulating material.

Magnesium salts are encountered in a small amount in all soils and are needed for plant nutrition because magnesium is contained in chlorophyll.

97. Calcium

Calcium is one of the most widespread elements in nature. Its content in the Earth's crust is about 3% (mass). It occurs in numerous deposits of limestones and chalk, and also of marble, which are all natural varieties of calcium carbonate CaCO_3 . Also encountered in large amounts are gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, phosphorite $\text{Ca}_3(\text{PO}_4)_2$ and, finally, various calcium-containing silicates.

Metallic calcium is produced chiefly by the electrolysis of molten calcium chloride. The metal obtained contains an admixture of CaCl_2 . It is therefore remelted, and then distilled to produce highly pure calcium. Both processes are conducted in a vacuum.

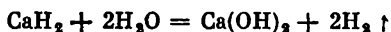
A certain amount of calcium is produced by the aluminothermic method of reduction. A method of producing calcium by the thermal dissociation of calcium carbide CaC_2 has also been developed.

Calcium is a ductile, quite hard white metal. It becomes coated with an oxide layer quite rapidly in air, and when heated burns with a bright reddish flame. Calcium reacts comparatively slowly with cold water, but rapidly displaces hydrogen from hot water to form the hydroxide. Calcium is a very active metal that readily combines with the halogens, sulphur, nitrogen, and reduces the oxides of many metals when heated with them.

The use of metallic calcium is associated with its high chemical activity. It is employed for reducing metals such as uranium, chromium, zirconium, cesium, and rubidium from their compounds, for removing oxygen and sulphur from steel and other alloys, for dehydrating organic liquids, and for absorbing the gases remaining in vacuum devices. Calcium is also used as a component of some lead alloys.

When heated in a stream of hydrogen, metallic calcium combines with the hydrogen to form a hydride.

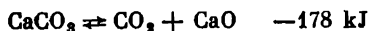
Calcium hydride CaH_2 is a white salt-like substance vigorously reacting with water with the liberation of hydrogen:



Owing to its ability to liberate a large amount of hydrogen, calcium hydride is sometimes used to prepare this gas (about 1000 litres of hydrogen are produced when one kilogram of calcium hydride reacts with water). It also finds use as an effective desiccant capable of removing water even from crystal hydrates.

Calcium oxide CaO is a white, very refractory substance melting only at a temperature of 2600°C . In engineering, calcium oxide is known as **unslaked** or **burnt lime**. The latter name indicates how it is prepared—by calcining or roasting calcium carbonate (in the form of limestone or chalk).

The roasting is performed in high shaft kilns. A kiln is charged with alternating layers of fuel and limestone and is fired from below. The roasting decomposes the calcium carbonate:



Since the concentrations of the substances in the solid phases are constant, we get the following expression for the equilibrium constant of this process:

$$K = [\text{CO}_2]$$

The concentration of a gas can be expressed by its partial pressure. Consequently, the latter equation signifies that equilibrium in the system being considered sets in at a definite partial pressure of the carbon dioxide. *The equilibrium partial pressure of a gas obtained in the dissociation of a substance is called the dissociation pressure of the substance.* The dissociation pressure of calcium carbonate at various temperatures has the following values:

Temperature, $^\circ\text{C}$	500	600	700	800	900	1000
Dissociation pressure:						
kPa	0.015	0.343	3.37	22.4	103.1	361.3
mmHg	0.11	2.35	25.3	168	773	2710

To violate equilibrium and cause the formation of a new amount of calcium oxide, it is necessary either to raise the temperature or remove part of the carbon dioxide formed, thus diminishing its partial pressure. If at a certain temperature the partial pressure of the carbon dioxide is kept at a lower value than the dissociation pressure, the calcium carbonate decomposes continuously. For this reason, an important role in roasting limestone is played by good ventilation of the kiln facilitating removal of the CO_2 and making it possible to conduct decomposition at a lower temperature.

If water is poured over burnt lime, it will be absorbed by the porous lumps of the lime and react with it with the liberation of a considerable amount of heat. Part of the water evaporates, while the lumps of lime break up into a fluffy mass of calcium hydroxide:

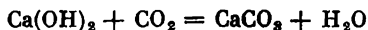


This operation is called **slaking**, and the product formed is called **slaked lime** in engineering.

Calcium hydroxide Ca(OH)_2 is a strong base sparingly soluble in water. One litre of water dissolves only 1.56 g of Ca(OH)_2 at 20°C . A saturated solution of calcium hydroxide is known as **lime water** and has an alkaline reaction. Lime water rapidly becomes

turbid in air because it absorbs carbon dioxide and forms insoluble calcium carbonate.

Slaked lime is widely used in building. Its mixture with sand and water is called mortar and is used for joining bricks in walls. Slaked lime is also used as a plaster. The lime hardens first because of the evaporation of water, and then as a result of the lime absorbing carbon dioxide from the air and forming calcium carbonate:



Owing to the small content of CO_2 in the air, the hardening process goes on very slowly, and since this is attended by the liberation of water, buildings erected with the use of such mortar remain damp inside for a long time.

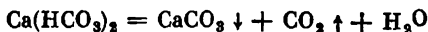
The most important calcium salts were treated when describing the relevant acids.

98. Hardness of Natural Water and Its Elimination

Because of the widespread occurrence of calcium, its salts are almost always present in natural water. Of the natural calcium salts, only gypsum is sparingly soluble in water, but if water contains carbon dioxide, calcium carbonate can also pass into solution as hydrogen carbonate $\text{Ca(HCO}_3)_2$.

Natural water containing a large amount of dissolved salts of calcium or magnesium is called hard water in contrast to soft water containing only a small amount or none of these salts.

The overall content of these salts in water is known as its total hardness. It is divided into carbonate and non-carbonate hardness. The former is due to the presence of calcium and magnesium hydrogen carbonates, and the second to the presence of salts of strong acids—calcium and magnesium sulphates or chlorides. When water with carbonate hardness is boiled for a long time, a precipitate appears in it that consists chiefly of CaCO_3 , and simultaneously CO_2 is evolved. Both these substances appear owing to the decomposition of calcium hydrogen carbonate:



This is why carbonate hardness is also referred to as temporary hardness. The latter is characterized quantitatively by the content of hydrogen carbonates removed from water when it is boiled for one hour. The hardness remaining after such boiling is called permanent.

The hardness of water in the USSR is expressed by the sum of the milliequivalents of calcium and magnesium ions contained in one litre of water. One milliequivalent of hardness corresponds to a content of 20.04 mg/l of Ca^{2+} or 12.16 mg/l of Mg^{2+} .

The hardness of natural water varies within broad limits. It is different in different basins, and changes during the year in the same river (it is minimum during high water). Table 11 gives the values of the water hardness in selected rivers of the USSR in summer.

Table 11.

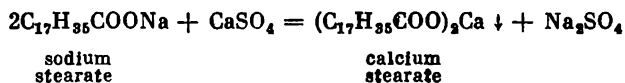
Water Hardness in Selected Rivers of the USSR

River	Place where hardness was measured	Water hardness, m-equiv/l		
		total	carbonate	non-carbonate
Volga	Volsk	5.9	3.5	2.4
Dnieper	Razumovka	3.7	3.2	0.5
Don	Aksakaiskaya	5.6	4.3	1.3
Yenisei	Krasnoyarsk	1.3	1.2	0.1
Moskva	Tatarovo	4.2	4.1	0.1
Neva	Ivanovskoe	0.5	0.5	0

The hardness of sea and ocean water is considerably higher than that of rivers and lakes. For instance, the water of the Black Sea has a total hardness of 65.5 m-equiv/l. The average hardness of the water in the world's oceans is 130.5 m-equiv/l (including 22.5 m-equiv/l falling to Ca^{2+} and 108 m-equiv/l falling to Mg^{2+}).

The presence of considerable amounts of calcium or magnesium salts in water makes it unsuitable for many technical purposes. For instance, when steam boilers are fed for a long time with hard water, their walls gradually become coated with a dense crust of scale. Such a crust even when one millimetre thick greatly lowers the transfer of heat to the water from the boiler walls and, consequently, leads to greater fuel consumption. In addition, it may cause the formation of blisters and cracks both in the boiler tubes and in the walls of the boiler itself.

Hard water does not produce a foam with soap because the soluble sodium salts of the fatty acids—palmitic and stearic—contained in soap transform into insoluble calcium salts of the same acids:



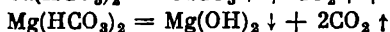
Hard water cannot be employed in some technological processes, for example in dyeing.

The above examples show the need of removing calcium and magnesium salts from water used for technical purposes. The removal of these salts, known as water softening, is part of a system of

water preparation—the treatment of natural water used for steam boiler feeding and for various technological processes.

In the course of preparation, water is freed of coarsely dispersed and colloidal impurities and of dissolved substances. Suspended and colloidal particles are removed by coagulation by salts added to the water [generally $\text{Al}_2(\text{SO}_4)_3$] followed by filtration.

Precipitation and ion exchange methods are employed for water softening. In the former method, the Ca^{2+} and Mg^{2+} cations are transferred to sparingly soluble compounds that precipitate. This is achieved either by boiling the water or chemically—by introducing the relevant reagents into the water. In boiling, the calcium and magnesium hydrogen carbonates transform into CaCO_3 and $\text{Mg}(\text{OH})_2$:



as a result of which only the carbonate hardness is eliminated.

In the chemical method of precipitation, lime or soda is most often used as the precipitant. All the calcium and magnesium salts are precipitated here [also in the form of CaCO_3 and $\text{Mg}(\text{OH})_2$].

To eliminate hardness by the ion exchange method (see Vol. 1, Sec. 110), or **cation exchange**, water is passed through a bed of a cation exchanger. The Ca^{2+} and Mg^{2+} cations in the water are exchanged for the Na^+ cations in the exchanger used. It is sometimes necessary to remove not only Ca^{2+} and Mg^{2+} cations from water, but also other cations and anions. In these cases, the water is passed consecutively through a cation exchanger containing hydrogen ions in an exchange form (an H-cation exchanger) and an anion exchanger containing hydroxide ions (an OH-anion exchanger). As a result, the water is freed both of cations and of anions of salts. Such water treatment is called **desalination** (desalting).

When an ion exchange process reaches equilibrium, the ion exchanger stops functioning—it loses its ability to soften water. But any ion exchanger is easily regenerated. For this purpose, a concentrated solution of NaCl (Na_2SO_4) or HCl (H_2SO_4) is passed through a cation exchanger. The Ca^{2+} and Mg^{2+} ions emerge into the solution, while the cation exchanger is again saturated with Na^+ or H^+ ions. To regenerate an anion exchanger, it is treated with a solution of an alkali or soda (the latter owing to the hydrolysis of the carbonate ion also has an alkaline reaction). As a result, the absorbed anions are again displaced into the solution, and the anion exchanger is saturated with OH^- ions.

99. Strontium. Barium

Strontium and barium occur in nature chiefly as sulphates and carbonates, forming the minerals celestite SrSO_4 , strontianite SrCO_3 , barite BaSO_4 , and witherite BaCO_3 . The content of strontium and

barium in the Earth's crust is respectively 0.04 and 0.05% (mass), i.e. considerably smaller than that of calcium.

Metallic strontium and barium are very active, rapidly oxidize in air, react quite vigorously with water (especially barium), and combine directly with many elements.

Strontium and barium oxides SrO and BaO are similar to calcium oxide. Both metals also form peroxides. Barium peroxide BaO_2 is obtained when barium oxide is heated in air to about 500°C . At a high temperature, it again decomposes into the oxide and oxygen. Barium peroxide, like sodium peroxide, is used for bleaching.

Strontium and barium hydroxides Sr(OH)_2 and Ba(OH)_2 are strong bases that dissolve in water better than calcium hydroxide: one litre of water at 20°C dissolves 8 g of strontium hydroxide and 38 g of barium hydroxide. A saturated solution of barium hydroxide is known as **baryta water** and is often used as a reagent.

Strontium and barium salts resemble those of calcium. The carbonates and sulphates SrCO_3 , BaCO_3 , SrSO_4 , and BaSO_4 are very sparingly soluble in water and precipitate from a solution in which strontium or barium ions encounter CO_3^{2-} or SO_4^{2-} ions. This is taken advantage of in analysis for separating strontium and barium from other metals.

The three metals can be distinguished from one another by the colour which their volatile salts impart to a non-luminous flame. Calcium salts colour a flame brick red, strontium salts—carmine, and barium salts—yellowish green.

SECONDARY SUBGROUP

The elements of this subgroup—**zinc, cadmium, and mercury**—have two electrons in the outer layer of an atom and eighteen in the next-to-last one. The configuration of the two outer electron shells of their atoms can be expressed by the formula $(n - 1) s^2 (n - 1) p^6 (n - 1) d^{10} ns^2$.

Table 12 gives selected properties of these metals.

The reducing properties of the zinc subgroup elements are considerably weaker than those of the main subgroup elements. This is explained by the smaller size of the atoms and, accordingly, by the higher ionization energies of these elements in comparison with the relevant elements of the main subgroup (compare the data of Tables 11 and 12).

In the atoms of zinc, cadmium, and mercury, as in the atoms of the copper subgroup elements, the d sublevel of the next-to-last electron layer is completely filled. But in the zinc subgroup elements, this sublevel is already quite stable, and the removal of electrons from it requires a lot of energy. Therefore, the elements

Table 12'

Selected Properties of Elements of the Secondary
Subgroup of Group II

	Zn	Cd	Hg
Configuration of outer and preceding electron layers of atom	$3s^2 3p^6 3d^{10} 4s^2$	$4s^2 4p^6 4d^{10} 5s^2$	$5s^2 5p^6 5d^{10} 6s^2$
Atomic radius, nm	0.139	0.156	0.160
Ionization energy			
$E \rightarrow E^+$, eV	9.39	8.99	10.44
$E \rightarrow E^{2+}$, eV	17.96	16.91	18.75
Radius of ion E^{2+} , nm	0.083	0.099	0.112
Standard enthalpy of atomization of metal at 25 °C, kJ per mole of atoms	130.5	111.7	61.5
Density, g/cm ³	7.13	8.65	13.546*
Melting point, °C	419.5	321.0	-38.89
Boiling point, °C	906	767	356.66
Standard electrode potential of process $E^{2+} + 2e^- = E$, V	-0.763	-0.403	0.850

* At 20 °C

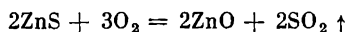
being considered exhibit an oxidation state of +2 in their compounds. Mercury, in addition, forms compounds in which its oxidation state is +1. But as will be shown on a later page (see Sec. 102), in these compounds too mercury should be considered divalent.

A feature of the zinc subgroup elements bringing them closer to those of the copper subgroup is their inclination to complexing.

100. Zinc (Zincum)

The chief natural compounds of zinc from which it is extracted are the minerals **smithsonite** or **dry-bone ore** $ZnCO_3$ and **zinc blende** or **sphalerite** ZnS . The total zinc content in the Earth's crust is about 0.01 % (mass).

Most zinc ores contain small amounts of zinc, therefore they are first concentrated to produce **zinc concentrate**. The latter is roasted to convert zinc sulphide to the oxide:



Roasting is performed in multihearth ovens or shaft kilns. Lately the roasting of zinc ores in a "fluidized bed" has come into great favour.

The method of processing finely comminuted solids in a fluidized bed has found widespread application in various branches of industry. It consists in the following. Air (or a gas) is blown from below through a layer of a powdered material on a grate with a velocity such that its jets penetrate into the material and intensively mix it, bringing it into a "fluidized" state, as it were.

Owing to the close contact of the solid material with the gas, chemical reactions proceed at a high rate in a fluidized bed. The use of roasting in a fluidized bed increases the output of roasting kilns three or four times with a more complete extraction of the zinc from the concentrate.

The method is very effective in roasting sulphide ores and concentrates, in the sublimation of comparatively volatile metals, and in the roasting, cooling, and drying of various substances.

The zinc is extracted from the roasted concentrate by reducing it with coke and distilling the zinc vapour formed.

Another method of reducing zinc is its electrolytic separation from its sulphate. The latter is produced by treating roasted concentrates with sulphuric acid.

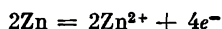
Zinc is a white metal with a bluish gray lustre. It is quite brittle at room temperature, but at 100-150 °C it bends well and can be rolled into sheets. When heated to above 200 °C, zinc becomes very brittle. In air, it becomes coated with a thin layer of the oxide or basic carbonate that prevents its further oxidation. Water does not virtually act on zinc although it is far ahead of hydrogen in the electromotive series. The explanation is that the hydroxide formed on the surface of zinc when it reacts with water is virtually insoluble and prevents the further course of the reaction. In dilute acids, however, zinc readily dissolves to form the corresponding salts. In addition, zinc, like beryllium and other metals forming amphoteric hydroxides, dissolves in alkalies. If zinc is heated greatly in air, its vapour ignites and burns with a greenish white flame, forming ZnO.

Zinc has a very great variety of applications. A considerable part of it goes to apply coatings to iron and steel articles intended for service in atmospheric conditions or in water. Zinc coatings provide a good protection of the basic metal against corrosion for many years. But they are not effective in highly humid air with considerable temperature fluctuations, and also in sea water. Alloys of zinc with aluminium, copper, and magnesium have found a broad industrial application. Zinc forms an important group of alloys—brasses—with copper (see p. 241). A considerable amount of zinc is used for the manufacture of galvanic cells.

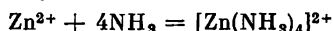
Manganese-Zinc Cell. Of all the galvanic cells used at present, manganese-zinc ones are in the greatest favour. There are several varieties of these cells, but they are all based on an oxidation-reduc-

tion reaction between zinc and manganese dioxide. In elements of this system, one electrode is of zinc and the other, of MnO_2 . Both electrodes are in an ammonium chloride solution.

During operation of the cell, the zinc becomes oxidized:



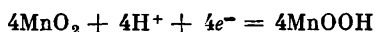
Part of the zinc ions formed combine with ammonia molecules into a complex ion:



Ammonia molecules form in the solution owing to hydrolysis of the ammonium ion (see Vol. 1, p. 276):



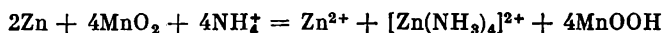
The electrons produced in the oxidation of the zinc pass via the external circuit to the manganese dioxide, which is reduced to yield several products. The compound MnOOH , in which the oxidation number of the manganese is +3, is produced in the greatest amount:



Hence, the zinc electrode of the cell is the anode and is charged negatively, while the MnO_2 electrode is the cathode and is charged positively.

The NH_4^+ and Cl^- ions during operation of the cell travel in directions due to the processes occurring at the electrodes. Since at the zinc electrode, the zinc cations emerge into the solution, while at the cathode the solution continuously loses H^+ cations, in the produced electric field the NH_4^+ ions migrate towards the cathode, and the Cl^- ions towards the anode. Consequently, the solution in all its parts remains electrically neutral.

If we summate the last four equations corresponding to the individual processes occurring in the operation of a cell, we get the net equation of the oxidation-reduction reaction proceeding in it:

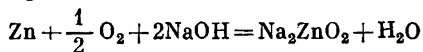


Manganese-zinc cells do not contain a solution in the ordinary meaning of this word. The NH_4Cl solution needed for their functioning in some designs has the consistency of a paste, and in others impregnates porous cardboard placed between the electrodes. This is the reason why these galvanic cells are called **dry cells**.

Dry cells are widely used as sources of current for communication installations, various instruments, and flashlights.

Air-Zinc Cell. Here zinc is the negative electrode, and the oxygen of the air (the pores of an electrode made from a mixture of activated carbon and graphite are filled with air) is the positive one. The oxygen diffuses to the electrode-solution interface. Solutions of NaOH or NH_4Cl are used as the electrolyte.

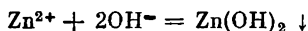
During the operation of such a cell, an oxidation-reduction reaction proceeds in it, which for an alkaline electrolyte is expressed by the equation:



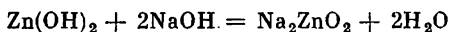
The mechanical and corrosion properties of zinc depend on the presence in it of small amounts of other metals. For example, an addition of iron increases the brittleness of zinc and its alloys and makes their working more difficult. It also sharply increases the rate of corrosion of zinc in acids. This is why high-quality zinc alloys contain very small amounts of additions of other metals. For instance, the amount of lead in them must never exceed 0.01%, and of iron, 0.1%.

Zinc oxide ZnO is a fluffy white powder that turns yellow when heated, but again becomes white when cooled. Zinc oxide is used in the manufacture of white oil paint (zinc white), in medicine and cosmetics (for preparing various ointments). A considerable portion of the zinc oxide produced is used as a filler of rubber.

Zinc hydroxide Zn(OH)_2 appears as a white precipitate when solutions of zinc salts are reacted with an alkali:

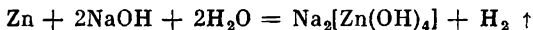


The precipitate readily dissolves in acids to form zinc salts and in an excess of alkalies to form **zincates**. Zinc hydroxide is thus an amphoteric compound. For instance, the following reaction proceeds with NaOH :

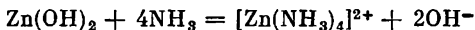


Like the formation of beryllates from beryllium hydroxide (p. 284), the formation of zincates is attended not only by the replacement of the hydrogen in Zn(OH)_2 by a metal, but also by the attachment of hydroxide ions. Particularly, hydroxozincates corresponding to the formulas $\text{Na}_2[\text{Zn(OH)}_4]$ and $\text{Ba}_2[\text{Zn(OH)}_6]$ have been separated in the solid state.

The dissolving of metallic zinc in alkalies is also attended by the formation of hydroxozincates, for example:



Zinc hydroxide also dissolves in an aqueous solution of ammonia and forms the complex ions $[\text{Zn(NH}_3)_4]^{2+}$:



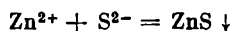
Zinc hydroxide is a weak electrolyte. Therefore all zinc salts, including zincates, become hydrolyzed in water.

Zinc Sulphate ZnSO_4 . This salt separates from an aqueous solution as a crystal hydrate of the composition $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and in this form is called **white vitriol**. It is used in dyeing and cotton

printing, in galvanic zinc-plating (as the main component of the electrolyte), in medicine, and is also the starting material for preparing other zinc compounds.

Zinc chloride ZnCl_2 is difficult to obtain in the anhydrous state. It usually contains about 5% of water and the basic chloride. A ZnCl_2 solution is used to pickle metals; in soldering, it facilitates the removal of oxides from the surface of a metal at the moment of soldering. Ammonium tetrachlorozincate $(\text{NH}_4)_2[\text{ZnCl}_4]$ (or $\text{ZnCl}_2 \cdot 2\text{NH}_4\text{Cl}$) is used for the same purpose in soldering and welding.

Zinc sulphide ZnS is one of the few sulphides having a white colour. It is prepared when alkali metal sulphides or ammonium sulphide react with zinc salts:



Zinc sulphide, and also zinc oxide are among the substances that **luminesce**—emit cold light under the action of radiant energy or electrons on them. Luminescence is widely used in science and engineering. For instance, of great importance is luminescence analysis, luminescent lamps are employed for lighting, and luminescent screens are the most important part of cathode-ray tubes.

Luminescence analysis is based on the different nature of glowing of different substances. It allows us to establish the presence of very small amounts of substances in mixtures, and also detect differences between objects which seem to be identical in visible light. It helps to sort glass and seeds, and detect microflaws in metal articles. It is employed in prospecting for bitumen and petroleum deposits and for uranium ores. Luminescence analysis plays an important role in forensic medicine and criminology, making it possible to establish the nature of various spots, and detect the falsification of documents and cryptography. The sensitivity of this kind of analysis is very high. In addition, there is no need of destroying the object being analysed, which is sometimes very important.

In luminescent daylight lamps, the mercury vapour in them, when a current is passed through it, emits ultraviolet radiation, which causes glowing of the substances applied in a thin coat to the inner surface of the lamp. These substances—luminophors—can be selected so that their radiation as regards its spectral composition approaches daylight.

Of tremendous importance is the application of luminophors in various cathode-ray tubes: in cathode oscillographs, television sets, etc. The screens of television sets are usually made of zinc sulphide.

101. Cadmium

Cadmium resembles zinc in its properties and is usually contained in zinc ores as an admixture. It is much inferior to zinc in its occurrence; the cadmium content in the Earth's crust is only about $10^{-50}\%$ (mass).

Cadmium is prepared from zinc production residues by treating the latter with sulphuric acid with the following recovery of the metallic cadmium by zinc:



The product is refined by dissolving it in dilute sulphuric acid and subjecting it to electrolysis.

Cadmium is a silvery soft, malleable, ductile metal. It is below zinc in the electromotive series, but above hydrogen and displaces the latter from acids. Since $\text{Cd}(\text{OH})_2$ is a weak electrolyte, cadmium salts become hydrolyzed, and their solutions have an acid reaction.

Cadmium greatly absorbs slow neutrons. This is why cadmium rods are used in nuclear reactors for controlling the rate of the chain reaction. Cadmium is used in alkaline accumulators (see Sec. 130) and is a component of some alloys. For example, copper alloys containing about 1% Cd (cadmium bronze) are used for making telegraph, telephone, and trolleybus wires because these alloys have a greater strength and wear resistance than copper. A number of fusible alloys, for example those used in automatic fire extinguishers, contain cadmium. Notwithstanding its comparatively high cost, cadmium is used for **cadmium-plating** steel articles because its surface has an oxide film with a protective action. Cadmium-plating is more effective than zinc-plating in sea water and in some other conditions.

When strongly heated, cadmium burns, transforming into brown **cadmium oxide** CdO .

Cadmium hydroxide $\text{Cd}(\text{OH})_2$, unlike zinc hydroxide, does not have appreciably expressed acid properties and does not virtually dissolve in alkalis.

Among the salts of cadmium, we shall note **cadmium sulphide** CdS that is deposited in the form of a yellow precipitate from solutions of cadmium salts when reacted with hydrogen sulphide. Cadmium sulphide goes to manufacture yellow paint and coloured glass.

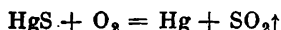
All cadmium compounds soluble in water and in dilute acids are poisonous. It is also very dangerous to inhale air containing a cadmium oxide "smoke".

102. Mercury {Hydrargyrum}

Mercury is scarce in nature. The Earth's crust contains only about $10^{-60}\%$ (mass) of it. Inclusions of native mercury are sometimes encountered in rocks, but it occurs in nature chiefly in the form

of the bright red mercury sulphide HgS , called **cinnabar**. This mineral is used to make red paint.

Mercury is produced from cinnabar by roasting the ore. The mercury separates as a vapour and condenses in a cooled receiver:



Mercury is the only metal that is liquid at room temperature. It is widely used in the chemical industry: as a cathode in the electrolytic production of sodium hydroxide and chlorine, and as a catalyst in the preparation of many organic compounds and in dissolving uranium slugs (in atomic power engineering). It is employed in the manufacture of daylight lamps (see Sec. 100), quartz lamps, manometers, and thermometers. In mining, mercury is used to separate gold from non-metallic impurities.

Mercury can dissolve many metals to form liquid or solid alloys called **amalgams**. A chemical compound of mercury with the relevant metal is sometimes obtained.

Sodium amalgam has found great favour as a reducing agent. Tin and silver amalgams are used for filling teeth.

Gold amalgam is formed especially readily, and for this reason gold articles must not be allowed to come into contact with mercury. Iron does not form an amalgam, hence mercury can be transported in steel vessels.

Mercury usually contains other metals as impurities. The major part of the impurities can be removed by agitating mercury with a solution of mercury(II) nitrate. The metals ahead of mercury in the electromotive series (which include most metals) pass into the solution and displace an equivalent amount of mercury from it. Complete refining of mercury is achieved by its repeated distillation, best of all under a diminished pressure.

Mercury vapour is very toxic and may cause serious poisoning. Even the negligible amount of its vapour forming at room temperature is enough for this to happen. This is why great care must be taken in any work with mercury. Do not keep vessels with mercury open, and perform all work with it on enamelled or iron trays. Mercury spilled onto the floor is extremely dangerous. In falling, it breaks up into a multitude of small droplets that get into cracks and can poison the air for a long time. Therefore, if mercury has been spilled onto a floor, it must be immediately gathered with the aid of a vacuum cleaner or of a pipette with a rubber bulb. Special reagents can also be used for removing mercury, known as demercurizers. Examples of the latter are sulphur powder, a 20% solution of FeCl_3 , an emulsion of mineral oil and water containing powdered sulphur and iodine, and a 10% solution of KMnO_4 acidified with hydrochloric acid.

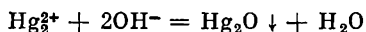
Among the zinc subgroup metals, mercury is the least active owing to the high ionization energy of its atoms (see Table 12). Hydrochloric and dilute sulphuric acids, and also alkalis do not react with mercury. It dissolves readily in nitric acid. Concentrated sulphuric acid dissolves mercury when heated.

Mercury is not oxidized in air at room temperature. Upon prolonged heating to a temperature close to its boiling point, mercury combines with the oxygen of the air to form red **mercury(II) oxide** HgO , which when heated to a higher temperature again decomposes into mercury and oxygen. In this compound, the oxidation number of mercury is +2. Mercury also has another oxide—**mercury(I) oxide** Hg_2O , in which its oxidation state is +1.

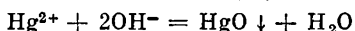
In all mercury(I) compounds, the mercury atoms are bonded to one another, forming divalent groups $-\text{Hg}_2-$ or $-\text{Hg}-\text{Hg}-$.

Consequently, mercury is also divalent in these compounds, but one valence unit of each mercury atom is used here for a bond with another mercury atom. This bond is also retained in solutions of mercury(I) salts containing mercury ions. Thus, the composition of mercury(I) salts containing a monovalent acid residue R should be depicted not by the empirical formula HgR , but by the formula Hg_2R_2 (for instance, Hg_2Cl_2).

One of mercury's features is that no hydroxides are known for it. When their formation could be expected, anhydrous oxides are obtained. For instance, when alkalis react with solutions of mercury(I) salts, a brownish black precipitate of mercury(I) oxide is obtained:

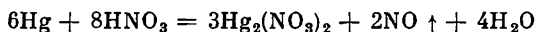


In exactly the same way, alkalis precipitate **mercury(II) oxide** from solutions of mercury(II) salts:

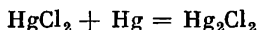


The precipitate formed is yellow, but when heated transforms into the red modification of mercury(II) oxide.

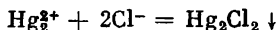
Mercury(I) nitrate $\text{Hg}_2(\text{NO}_3)_2$ is one of the few soluble salts of mercury(I). It is obtained when dilute cold nitric acid is reacted with excess mercury:



Mercury(I) chloride Hg_2Cl_2 or **calomel** is a white powder insoluble in water. It is prepared by heating a mixture of HgCl_2 and mercury:

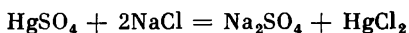


Calomel can also be prepared by reacting hydrogen chloride or sodium chloride with soluble mercury(I) salts:



Mercury(II) nitrate $\text{Hg}(\text{NO}_3)_2$ is prepared when excess hot nitric acid reacts with mercury. It dissolves well in water. In dilute solutions in the absence of free acid, it hydrolyzes to form a white precipitate of the basic salt $\text{HgO} \cdot \text{Hg}(\text{NO}_3)_2$. When heated with a large amount of water, the basic salt also decomposes, mercury(II) oxide being a product.

Mercury(II) chloride, or **corrosive sublimate** HgCl_2 can be prepared by the direct reaction of mercury with chlorine. It is a colourless substance comparatively poorly soluble in cold water (6.6 g in 100 g of water at 20 °C). With elevation of the temperature, however, the solubility of mercury(II) chloride grows greatly, reaching 58 g in 100 g of water at 100 °C. It crystallizes from a solution as long lustrous prisms. This salt is customarily prepared by heating mercury(II) sulphate with sodium chloride:

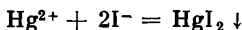


The mercury(II) chloride sublimes. This is why it has also been named corrosive sublimate.

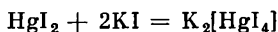
An aqueous solution of mercury(II) chloride does not virtually conduct electricity. It is thus one of the few salts that almost does not ionize in an aqueous solution. As indicated in Vol. 1, p. 161, the explanation is the high polarizing power of the Hg^{2+} ion.

Mercury(II) chloride, like all soluble mercury salts, is a strong poison. It is used for treating seeds, tanning leather, preparing other mercury compounds, for dyeing fabrics, as a catalyst in organic synthesis, and as a disinfectant (p. 31).

Mercury(II) iodide HgI_2 precipitates as a beautiful orange-red solid when a potassium iodide solution is reacted with a mercury(II) salt:



The salt readily dissolves in excess potassium iodide, forming a colourless solution of the complex salt $\text{K}_2[\text{HgI}_4]$:



Mercury(II) sulphide HgS occurs in nature (see above). It can be obtained artificially as a black substance by the direct combination of sulphur with mercury or by reacting hydrogen sulphide with solutions of mercury(II) salts.

When heated without the access of air, black mercury(II) sulphide transforms into the red crystalline modification—cinnabar.

THIRD GROUP OF THE PERIODIC TABLE

The third group of the periodic table consists of a very large number of chemical elements because in addition to the elements of the main and secondary subgroups it includes the elements with the atomic numbers 58-71 (lanthanides) and with the atomic numbers 90-103 (actinides). We shall consider the lanthanides and actinides together with the secondary subgroup elements.

MAIN SUBGROUP

The elements of the main subgroup of Group three—**boron, aluminium, gallium, indium, and thallium**—are characterized by the presence of three electrons in the outer electron layer of the atom. The next-to-last electron layer of the boron atom contains two electrons, of the aluminium atom—eight, and of gallium, indium and thallium—eighteen electrons. Selected properties of these elements are given in Table 13.

Table 13

Selected Properties of Boron, Aluminium, and Their Analogues

	B	Al	Ga	In	Tl
Configuration of outer electron layer of atom	$2s^2 2p^1$	$3s^2 3p^1$	$4s^2 4p^1$	$5s^2 5p^1$	$6s^2 6p^1$
Atomic radius, nm	0.091	0.143	0.139	0.166	0.171
Ionization energy					
$E \rightarrow E^+$, eV	8.30	5.99	6.00	5.79	6.11
$E^+ \rightarrow E^{2+}$, eV	25.15	18.8	20.5	18.9	20.4
$E^{2+} \rightarrow E^{3+}$, eV	37.9	28.4	30.7	28.0	29.8
Radius of ion E^{3+} , nm	0.020	0.057	0.062	0.092	0.105
Standard enthalpy of atomization, kJ per mole of atoms	561.6	329.1	272.9	238.1	181.0
Density, g/cm ³	2.34	2.70	5.90	7.31	11.85
Melting point, °C	2075	660	29.8	156.4	304
Boiling point, °C	3700	2500	2205	2000	1475

The metallic properties of the elements being considered are weaker than those of the relevant elements of the main subgroups of group two and especially of group one, while in boron non-metallic properties predominate. In compounds, they exhibit the oxidation state +3. With a growth in the atomic mass, however, lower oxidation states also appear. The most stable compounds of the last

element of the subgroup—thallium—are those in which its oxidation state is $+1$.

With an increase in the atomic number, the metallic properties of the elements being considered, as in the other main subgroups, appreciably grow. For instance, boron oxide is acid in nature, aluminium, gallium, and indium oxides are amphoteric, while thallium(III) oxide is basic.

From a practical viewpoint, the most important of the Group III elements are boron and aluminium.

103. Boron (*Borum*)

Boron is comparatively scarce in nature. Its total content in the Earth's crust is about $10^{-3}\%$ (mass).

The principal natural compounds of boron are boric acid H_3BO_3 and salts of boric acids, the most well known of which is borax $Na_2B_4O_7 \cdot 10H_2O$.

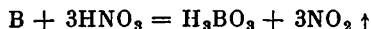
Although boron is in the third group of the periodic table, as regards its properties it has the greatest resemblance not to the other elements of this group, but to an element of Group IV—silicon. This is a manifestation of the diagonal similarity already mentioned when treating beryllium. For example, boron, like silicon, forms weak acids exhibiting no amphoteric properties, whereas $Al(OH)_3$ is an amphoteric base. Compounds of boron and silicon with hydrogen, unlike solid aluminium hydride, are volatile substances igniting spontaneously in the air. Like silicon, boron forms compounds with metals, many of which are distinguished by their great hardness and high melting point.

Free boron is prepared by reducing boric anhydride B_2O_3 with magnesium. The boron separates as an amorphous powder contaminated with impurities. Pure crystalline boron is prepared by the thermal decomposition or reduction of its halides, and also by the decomposition of the hydrogen compounds of boron. It is black, and among the elementary substances it is inferior in its hardness only to diamond.

Natural boron consists of two stable isotopes: ^{10}B and ^{11}B . The former greatly absorbs slow neutrons. This is why boron and its compounds are employed in nuclear engineering. They are used to make the control rods of reactors, and also as materials affording protection against neutron radiation.

In metallurgy, boron is used as an addition to steel and to some non-ferrous metal alloys. The addition of very small amounts of boron diminishes the grain size, which improves the mechanical properties of alloys. Also used is the surface saturation of steel articles with boron—**boriding**, which increases the hardness and resistance to corrosion.

Water does not react with boron. Concentrated sulphuric and nitric acids, however, oxidize it to boric acid. For example:



At room temperature, boron combines only with fluorine; it does not oxidize in air. If amorphous boron is heated to 700 °C, it ignites and burns with a reddish flame, transforming into the oxide with the evolution of a large amount of heat:



At a high temperature, boron combines with many metals to form **borides**, for instance, magnesium boride Mg_3B_2 . Many borides are very hard and chemically stable, retaining these properties at elevated temperatures. They are also characterized by refractoriness. For example, zirconium boride ZrB_2 melts at 3040 °C. Owing to these properties, the borides of some metals are used to manufacture components of jet engines and gas turbine blades.

When a mixture of boron and coal is heated, boron carbide B_4C is formed. It is a refractory substance (melting point about 2350 °C), very hard, and chemically stable. Boron carbide is used for processing hard alloys; it retains its mechanical properties at high temperatures.

Boron also reacts with halogens when heated and forms substances having the general formula BX_3 (where X stands for a halogen). As already indicated when considering the example of BF_3 (see Vol. 1, p. 143), in these compounds boron is in the state of sp^2 hybridization and forms with halogens plane molecules with angles of 120 degrees between the $\text{X}-\text{B}-\text{X}$ bonds.

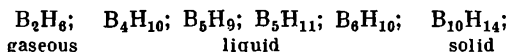
Boron halides, like other boron compounds having a non-polymeric structure, are electron-deficient (see p. 280). For example, the outer electron layer of the boron atom in a boron fluoride molecule contains only six electrons:



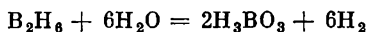
The boron atom in this state, consequently, can be an acceptor of an electron pair. Indeed, BF_3 forms a donor-acceptor bond with water, ammonia, and other substances; the complex anion BF_4^- is also known. In all such compounds, the covalence and the coordination number of boron equal four, while the boron atom is in the state of sp^3 hybridization and forms tetrahedral structures.

Hydrogen Borides (Boranes). When hydrochloric acid is reacted with magnesium boride Mg_3B_2 , a complex mixture of various hydrogen borides similar to hydrocarbons and silanes is obtained. The following hydrogen borides have been separated in the pure form

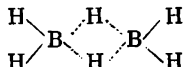
from this mixture:



The main product obtained in the reaction of magnesium boride with hydrochloric acid is **tetraborane** B_4H_{10} —a volatile liquid (boiling point $18^\circ C$) with a very unpleasant odour whose vapour ignites in air. When stored, tetraborane gradually decomposes to form the simplest of the hydrogen borides that have been obtained—**diborane** B_2H_6 . The latter is a gas condensing into a liquid at $-92.5^\circ C$. It does not ignite in the air, but like the other boranes, when reacted with water immediately decomposes with the detachment of hydrogen and the formation of boric acid H_3BO_3 :



The boron atoms in borane molecules are bonded to one another by hydrogen “bridges”, for instance:



The dotted lines in this formula show three-centre bonds: here the shared pair of electrons occupies a molecular orbital encompassing three atoms—a bridge hydrogen atom and both boron atoms. Such an orbital is formed owing to the overlapping of the $1s$ orbital of a hydrogen atom and the sp^3 hybrid orbitals of the two boron atoms (see Fig. 60). The four “terminal” hydrogen atoms are bonded to the boron atoms by conventional two-centre two-electron bonds. Thus, of the twelve valence electrons in the atoms forming a diborane

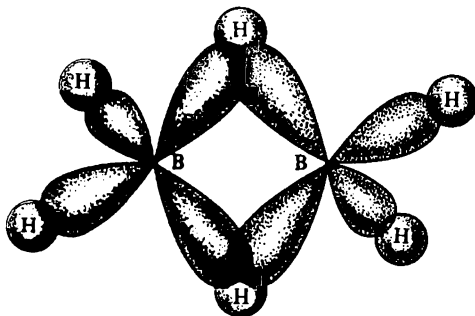


Fig. 60. Overlapping of the atomic orbitals in a diborane molecule

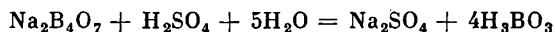
molecule, eight participate in the formation of two-centre B—H bonds, and four form two three-centre bonds B—H—B.

The oxygen compounds of boron are of the greatest practical significance.

Diboron trioxide, or **boric anhydride** B_2O_3 can be prepared either by the direct combination of boron with oxygen or by the calcination of boric acid. It is a colourless brittle vitreous body melting at about 300 °C. Diboron trioxide is very refractory and is not reduced by coal even when white-hot. It dissolves in water to form boric acid with the evolution of heat:



Boric, or **orthoboric acid** H_3BO_3 forms white crystals whose lustrous scales dissolve in hot water. Boric acid can be prepared by reacting sulphuric acid with a hot solution of sodium tetraborate $Na_2B_4O_7$:



When the solution is cooled, the boric acid crystallizes because it is only sparingly soluble in cold water.

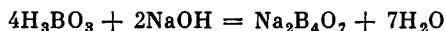
When a boric acid solution is boiled, the boric acid evaporates partly together with the water. This explains its presence in the water vapour escaping from fissures in the earth in volcanic localities.

Boric acid is a very weak acid (at 20 °C, $K_1 = 6 \times 10^{-10}$, $K_2 = 2 \times 10^{-13}$, and $K_3 = 2 \times 10^{-14}$).

Boric acid loses water when heated, transforming first into **metaboric acid** HBO_2 , and then into diboron trioxide B_2O_3 . Boric acid is used to prepare enamels and glazes, in the production of special grades of glass, in the paper and leather industries, and as a disinfectant.

The salts of boric acids—**borates**—are in their majority derivatives not of orthoboric acid H_3BO_3 , but of **tetraboric acid** $H_2B_4O_7$ and of other boric acids containing less water.

Sodium tetraborate, or **borax**, forms large colourless transparent crystals of the composition $Na_2B_4O_7 \cdot 10H_2O$, which readily effloresce in dry air. Borax is produced when boric acid reacts with sodium hydroxide:



Aqueous solutions of borax, owing to hydrolysis, have a strongly alkaline reaction.

When heated, borax loses its water of crystallization and melts. In the molten state, it dissolves oxides of various metals with the formation of double salts of metaboric acid, many of which have colours characteristic of each metal. This property of borax underlies its use in the welding, cutting, and soldering of metals. Borax finds great favour in the production of a fusible glaze for faience (pottery) and porcelain ware and especially for iron utensils (enamel). It is also used in the production of special grades of glass and as a fertilizer because small amounts of boron are needed by plants.

104. Aluminium

Aluminium is the most widespread metal in the Earth's crust. It is contained in clays, feldspars, micas, and many other minerals. The total content of aluminium in the Earth's crust is 8% (mass).

The basic raw material for the production of aluminium is **bauxite** containing from 32 to 60% of **alumina** Al_2O_3 . Important aluminium ores also include **alunite** $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 2\text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ and **nephelite** $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$.

The USSR has great reserves of aluminium ores. In addition to bauxites occurring in the Urals, in the Bashkirian SSR, and in Kazakhstan, an extremely rich source of aluminium is nephelite occurring together with apatite in the Khibiny Mountains. There are considerable reserves of aluminium ores in Siberia.

Aluminium was prepared for the first time by F. Wöhler in 1827, by reacting metallic potassium with aluminium chloride. Notwithstanding its widespread occurrence in nature, however, aluminium was one of the rare metals up to the end of the 19th century.

At present, aluminium is produced in enormous amounts from aluminium oxide Al_2O_3 (alumina) electrolytically. The alumina used for this purpose must be sufficiently pure because impurities are removed with great difficulty from the product. Purified Al_2O_3 is prepared by processing natural bauxite.

The production of aluminium is an intricate process involving great difficulties. The chief reactant—aluminium oxide—does not conduct electricity and has a very high melting point (about 2050 °C). For this reason, electrolysis is conducted with a molten mixture of cryolite* $\text{Na}_3[\text{AlF}_6]$ and aluminium oxide. The mixture, containing about 10% (mass) of Al_2O_3 , melts at 960 °C and has the optimal electrical conductance, density, and viscosity. To additionally improve these characteristics, AlF_3 , CaF_2 , and MgF_2 are added to the mixture. As a result, it becomes possible to conduct electrolysis at 950 °C.

An electrolyzer for melting aluminium is an iron housing lined inside with refractory brick. Its bottom (hearth) assembled of blocks of pressed coal is the cathode. The anodes (one or several) are installed on top. These are aluminium frames filled with coal briquettes. At modern works, the electrolyzers are installed in series, each series consisting of 150 or more units.

In electrolysis, aluminium is liberated at the cathode, and oxygen at the anode. The aluminium, which has a higher density than the initial melt, gathers at the bottom of the electrolyzer, whence

* Deposits of cryolite, a very important mineral for the aluminium industry, are extremely rare. This is why cryolite is generally produced artificially—by reacting aluminium hydroxide with hydrofluoric acid and then neutralizing the acid solution with soda.

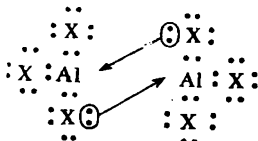
it is periodically tapped. As the metal is separated, new portions of alumina are added to the melt. The oxygen formed in electrolysis reacts with the carbon of the anode, which burns out forming CO and CO₂.

No aluminium was produced in prerevolutionary Russia. The first aluminium plant in the USSR (the Volkhov plant) was placed into service in 1932, while already in 1935, the country occupied the third place in the world in the production of aluminium.

The identical structure of the outer electron layer in boron and aluminium atoms is the reason why the properties of these elements are similar. For instance, both aluminium and boron are characterized by an oxidation state of only +3. When going from boron to aluminium, however, the atomic radius grows very significantly (from 0.091 to 0.143 nm), and, in addition, another intermediate eight-electron layer appears that screens the nucleus. All this leads to weakening of the bond of the outer electrons to the nucleus and to a reduction in the ionization energy of an atom (see Table 13). Consequently, the metallic properties of aluminium are much stronger than of boron. Nevertheless, the chemical bonds formed by aluminium with other elements are mainly of a covalent nature.

Another feature of aluminium (and of its analogues—gallium, indium, and thallium) in comparison with boron is the existence of free *d* sublevels in the outer electron layer of its atom. Consequently, the coordination number of aluminium in its compounds may not only be four, as in boron, but also six.

Aluminium compounds of the type AlE₃, like similar boron compounds, are electron-deficient: the outer electron layer of the aluminium atom has only six electrons in molecules of such compounds. For this reason, here the aluminium atom can be an acceptor of electron pairs. Particularly, aluminium halides form dimers having donor-acceptor bonds (in the formula, X is a halogen atom):



A glance at the formula shows that such dimer molecules contain two bridge halogen atoms each. The spatial structure of Al₂Cl₆ is shown schematically in Fig. 61. Aluminium halides exist as dimer molecules Al₂X₆ in melts and in vapours. According to tradition, however, their composition is usually expressed as AlX₃. Below we shall also adhere to this way of writing the formulas of aluminium halides.

Aluminium hydride AlH₃ is also an electron-deficient compound. But a hydrogen atom, unlike the halogen atoms in the AlX₃ mole-

cules, has no unshared electron pair and cannot play the role of a donor of electrons. Therefore, the individual AlH_3 molecules here are bonded with one another via bridge hydrogen atoms by means of three-centre bonds similar to those in the borane molecules (see the preceding section). The result is the formation of a solid polymer whose composition can be expressed by the formula $(\text{AlH}_3)_n$.

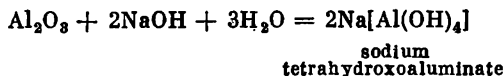
Aluminium is a silvery light-weight metal. It is readily extruded into a wire and rolled into thin sheets.

Aluminium does not change in air at room temperature, but only because its surface becomes covered with a thin oxide film having a very strong protective action. If this film is destroyed, for example by amalgamation of the aluminium, rapid oxidation of the metal occurs attended by appreciable heating.

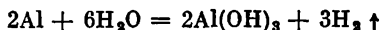
The standard electrode potential of aluminium is -1.663 V. Notwithstanding this great negative potential, aluminium, owing to the formation of a protective oxide film on its surface, does not displace hydrogen from water. But amalgamated aluminium, on which no dense oxide layer is formed, vigorously reacts with water, with the liberation of hydrogen.

Dilute hydrochloric and sulphuric acids readily dissolve aluminium, especially when heated. Greatly diluted and cold concentrated nitric acid does not dissolve it.

When aqueous solutions of alkalis react with aluminium, the oxide layer dissolves and aluminates are formed—salts containing aluminium in the anion:



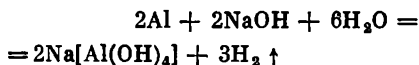
Aluminium deprived of its protective film, like amalgamated aluminium, reacts with water, displacing hydrogen from it:



The aluminium hydroxide reacts with excess alkali to form a hydroxoaluminate:



Doubling the last equation and adding it to the preceding one, we get the net equation of dissolving of aluminium in an aqueous solution of an alkali:



Aluminium dissolves appreciably in solutions of salts having

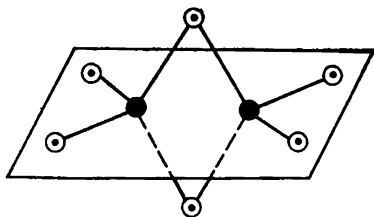


Fig. 61. Spatial structure of Al_2Cl_6 molecule:
the black circles depict aluminium atoms, the white ones—chlorine atoms

an acid or alkaline reaction owing to their hydrolysis, for example in a solution of Na_2CO_3 .

If an aluminium powder (or thin aluminium foil) is heated strongly, it ignites and burns with a blinding white flame, forming aluminium oxide.

The main application of aluminium is the production of alloys based on it. Alloying additions (for instance, copper, silicon, manganese, zinc, and magnesium) are introduced into aluminium chiefly to improve its strength. Widespread use has been found by duralumins, containing copper and magnesium, silumins, in which the main addition is silicon, and magnaliums (alloys of aluminium with from 9.5 to 11.5% of magnesium). The principal merits of all aluminium alloys are their low density (2.5 to 2.8 g/cm³), high strength (calculated per unit mass), satisfactory resistance to atmospheric corrosion, comparative cheapness, and the simplicity of production and processing. Aluminium alloys are employed in rocket engineering, in the aircraft, motor vehicle, ship-building, and instrument-making industries, in the manufacture of utensils, and in many other branches of industry. Aluminium alloys occupy the second place after steel and iron in the diversity of their applications.

Aluminium is one of the most favoured additions to alloys based on copper, magnesium, titanium, nickel, zinc, and iron.

Pure aluminium goes to manufacture chemical apparatus, electrical wires, and capacitors. Although the electrical conductivity of aluminium is lower than that of copper (about 60% of the latter), this is compensated by the light weight of aluminium allowing thicker wires to be made: an aluminium wire having the same electrical conductance as a copper one weighs only half of the latter.

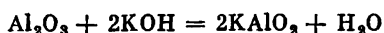
Of substantial importance is the use of aluminium for **calorizing** (or **aluminizing**), which consists in the saturation of the surface of steel or iron articles with aluminium to protect the parent metal from oxidation when strongly heated. In metallurgy, aluminium is used in the production of calcium, barium, lithium, and some other metals by aluminothermics (see Sec. 78).

Aluminium oxide Al_2O_3 or **alumina**, occurs in nature in the crystalline form as the mineral **corundum**. The latter is very hard. Its transparent crystals coloured red or blue by impurities are precious stones called **ruby** and **sapphire**. At present rubies are produced artificially by melting alumina in an electric furnace. They are used not so much as adornments as for technical purposes, for instance to manufacture components of high-precision instruments, jewels in watches and clocks, etc. Ruby crystals containing a small admixture of Cr_2O_3 are used as quantum generators—lasers, which create a directed beam of monochromatic radiation.

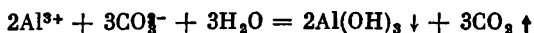
Corundum and its fine-grained variety containing a large amount of impurities—**emery**, are employed as abrasive materials.

Aluminium hydroxide $\text{Al}(\text{OH})_3$ forms a jelly-like precipitate when alkalies are reacted with solutions of aluminium salts; it readily forms colloidal solutions.

Aluminium hydroxide is a typical amphoteric hydroxide. With acids, it forms salts containing an aluminium cation, with alkalies it forms aluminates. When aluminium hydroxide reacts with aqueous solutions of alkalies or when metallic aluminium is dissolved in alkali solutions, the products, as mentioned above, are **hydroxo-aluminates**, for example $\text{Na}[\text{Al}(\text{OH})_4]$. When aluminium oxide is melted with the relevant oxides or hydroxides, however, the products are **metaaluminates**—derivatives of metaaluminic acid HAlO_2 , for example:



Both aluminium salts and aluminates become greatly hydrolyzed in solutions. Consequently, salts of aluminium and weak acids transform in solution into basic salts or are completely hydrolyzed. For example, the reaction of an aluminium salt with Na_2CO_3 in solution produces not aluminium carbonate, but aluminium hydroxide, and carbon dioxide is liberated:



Aluminium Chloride AlCl_3 . Anhydrous aluminium chloride is prepared by the direct reaction of chlorine with aluminium. It finds great favour as a catalyst in various organic syntheses. It dissolves in water with the evolution of a large amount of heat. Evaporation of the solution is attended by hydrolysis, the liberation of hydrogen chloride, and the production of aluminium hydroxide. If evaporation is conducted in the presence of excess hydrochloric acid, crystals of the composition $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ can be obtained.

As we have indicated on an earlier page, the chemical bonds formed by an aluminium atom are chiefly covalent. This affects the properties of the compounds it forms. For instance, at standard atmospheric pressure, anhydrous aluminium chloride sublimes already at 180°C , while at high pressures it melts at 193°C ; it does not conduct electricity in the molten state. Hence, molten AlCl_3 cannot be used for the electrolytic preparation of aluminium.

Aluminium sulphate $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ is obtained when hot sulphuric acid reacts with aluminium oxide or with kaolin. It is used in water purification (see p. 288), and also in the manufacture of certain grades of paper.

Alum $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is employed in large amounts for tanning hides, and as a mordant in dyeing cotton fabrics. In the latter case, its action is based on the fact that the aluminium hydroxide formed owing to hydrolysis of the alum is deposited in the fabric fibres in a finely dispersed state, adsorbs the dye, and firmly retains it on the fibre.

105. Gallium. Indium. Thallium

These elements are rare and do not occur in nature in considerable concentrations. They are chiefly produced from zinc concentrates after the zinc has been melted from them.

In the free state, these elements are silvery white soft metals with a low melting point. They are quite stable in air, do not decompose water, but readily dissolve in acids, and gallium and indium—also in alkalies. In addition to the maximum oxidation state of +3, they can also exhibit a lower one. Particularly, thallium is characterized by compounds where its oxidation state is +1.

The oxides and hydroxides of gallium(III) and indium(III) are amphoteric, while thallium hydroxide $Tl(OH)_3$ has only basic properties.

Thallium(I) compounds are similar, on the one hand, to compounds of the alkali metals, and on the other, to silver compounds. For instance, thallium(I) oxide Tl_2O vigorously combines with water to form a hydroxide corresponding to the formula $TlOH$ —a strong base well soluble in water.

Most thallium(I) salts readily dissolve in water, but the halides, like those of silver, are virtually insoluble and are distinguished by their light sensitivity. An exception is TlF , which like AgF is well soluble in water.

Metallic gallium is used to fill quartz thermometers employed for measuring high temperatures. Gallium melts at $29.8^\circ C$ and boils only at $2205^\circ C$, so that such thermometers allow temperatures up to $1000^\circ C$ and above to be measured. This is impossible when ordinary thermometers are used. The addition of gallium to aluminium yields alloys well lending themselves to hot working. Alloys of gallium with gold are used in jeweller's art and dentures.

Indium is used instead of silver for coating reflectors. Indium-coated reflectors do not tarnish with time, and therefore their coefficient of reflection remains constant. Indium is also used for coating bearing inserts and as a component of alloys used to make fuse links.

Gallium and indium are used in semiconductor electronics as additions to germanium and as intermetallic compounds with arsenic and antimony.

The applications of thallium and its compounds are small in magnitude, but quite diverse. Thallium halides are good transmitters of infrared rays. This explains their use in optical instruments operating in the infrared region of the spectrum. Thallium carbonate goes to make glasses having a high refractive power. Thallium is an ingredient of the substance forming a selenium rectifier electrode, and is the activator of many luminophors. Thallium sulphide is

employed in photoelectric cells. Metallic thallium is a component of many bearing, acid-resistant, and fusible alloys of lead.

Thallium and its compounds are very toxic.

SECONDARY SUBGROUP. LANTHANIDES. ACTINIDES

The elements of the secondary subgroup of group III and the family consisting of fourteen *f* elements with atomic numbers from 58 to 71 are very close to one another in their chemical and physico-chemical properties. These elements follow lanthanum in the periodic table and are therefore known as lanthanides. Sometimes, together with the elements of the secondary subgroup of group III, they are called the rare-earth metals.

The rare-earth metals generally occur together in nature. They form minerals that are solid solutions of related compounds of various metals. For example, one of the main sources of the rare-earth metals is the mineral monazite consisting chiefly of phosphates of cerium, lanthanum, yttrium, and other rare-earth metals. Hence, the same minerals are the natural starting material from which both the elements of the secondary subgroup of group III and the lanthanides are produced.

The actinides are a family of fourteen *f* elements with atomic numbers from 90 to 103 following actinium in the periodic table.

106. Scandium Subgroup

The secondary subgroup of group III includes the elements scandium, yttrium, lanthanum, and actinium. An atom of any of these elements contains two electrons in its outer electron layer and nine electrons in the preceding layer. The structure of these two electron layers can be expressed by the formula $(n-1)s^2(n-1)p^6(n-1)d^1ns^2$. Each of these elements begins the relevant decade of *d* elements. Some of their properties are given in Table 14. The oxidation state of the scandium subgroup elements is +3 in most of their compounds.

Scandium, yttrium and lanthanum are contained in the Earth's crust in amounts of the order of $10^{-3}\%$ (mass). The amount of actinium is much smaller [of the order of $10^{-9}\%$ (mass)] because both of its natural isotopes— ^{227}Ac and ^{228}Ac —are radioactive.

In the free state, the elements of the scandium subgroup are silvery metals with a high melting point. Their metallic properties are more pronounced than in the main subgroup elements. They dissolve in dilute hydrochloric, nitric, and sulphuric acids, and when heated react with most of the non-metals.

Table 14

Selected Properties of Elements of Secondary Subgroup of Group III

	Sc	Y	La	Ac
Configuration of outer and preceding electron layers of atom	$3s^2 3p^6 3d^1 4s^2$	$4s^2 4p^6 4d^1 5s^2$	$5s^2 5p^6 5d^1 6s^2$	$6s^2 6p^6 6d^1 7s^2$
Atomic radius, nm	0.164	0.181	0.187	0.203
Ionization energy				
$E \rightarrow E^+, \text{eV}$	6.56	6.22	5.58	5.1
$E^+ \rightarrow E^{2+}, \text{eV}$	12.8	12.24	11.06	12.1
$E^{2+} \rightarrow E^{3+}, \text{eV}$	24.75	20.5	19.17	...
Radius of ion E^{3+} , nm	0.083	0.097	0.104	0.111
Density, g/cm ³	3.02	4.48	6.16	10.1
Melting point, °C	1539	1528	920	1040±50
Boiling point, °C	About 2850	About 3300	3450	About 3300

The oxides of the elements of this subgroup are refractory white substances. The hydroxides exhibit basic properties that become more pronounced when going down the series Sc-Y-La. For instance, scandium salts are hydrolyzed to a considerable extent, whereas lanthanum salts are virtually not hydrolyzed: $\text{La}(\text{OH})_3$ is a strong base.

The fields of application of scandium are limited. But at present, ways of using scandium compounds in electronics are being outlined. Particularly, certain ferrites (see p. 366) containing small amounts of scandium oxide are used in high-speed computers. Metallic scandium is employed in electrovacuum engineering as a good getter (a non-disintegrating absorber of gases).

Yttrium oxide is also used in the production of ferrites. Ferrites containing yttrium are used in hearing aids, and in the memory cells of computers. The yttrium isotope ^{90}Y is employed in medicine.

Lanthanum is chiefly used in a mixture with lanthanides (see the following section).

107. Lanthanides

The lanthanide family includes 14 *f* elements following lanthanum in the periodic table:

58 Cerium Ce ... $4f^2 5s^2 5p^6 6s^2$	59 Praseodymium Pr ... $4f^3 5s^2 5p^6 6s^2$	60 Neodymium Nd ... $4f^4 5s^2 5p^6 6s^2$	61 Promethium Pm ... $4f^5 5s^2 5p^6 6s^2$
62 Samarium Sm ... $4f^6 5s^2 5p^6 6s^2$	63 Europium Eu ... $4f^7 5s^2 5p^6 6s^2$	64 Gadolinium Gd ... $4f^7 5s^2 5p^6 5d^1 6s^2$	65 Terbium Tb ... $4f^8 5s^2 5p^6 6s^2$

66 Dysprosium Dy ... $4f^{10}5s^26p^66s^2$	67 Holmium Ho ... $4f^{11}5s^25p^66s^2$	68 Erbium Er ... $4f^{12}5s^25p^66s^2$
69 Thulium Tm ... $4f^{13}5s^25p^66s^2$	70 Ytterbium Yb ... $4f^{14}5s^25p^66s^2$	71 Lutetium Lu ... $4f^{14}5s^25p^65d^16s^2$

An increase in the atomic number of the elements of this family is attended by filling of the sublevel of the third electron layer from the outer one (the $4f$ sublevel) with electrons. The configuration of the outer layer, and in most elements also of the preceding one, remains unchanged. This is why all the lanthanides are very close to one another in their chemical properties.

The electrons fill the $4f$ instead of the $5d$ sublevel because in this case they have less energy. The difference between the energies of the $4f$ and $5d$ states, however, is very small. For this reason, one of the $4f$ electrons (and in some cases, for instance in cerium, two $4f$ electrons) is easily excited, passes over to the $5d$ sublevel, and thus becomes a valence electron. Consequently, the lanthanides in most of their compounds have an oxidation state of $+3$, and not $+2$. This circumstance explains the closeness of the properties of the lanthanides to those of the scandium subgroup elements.

It was indicated in Vol. 1, Sec. 34, that within the limits of one period a growth in the atomic number of elements is attended by decreasing of their dimensions. This law is observed not only in the elements of the main subgroups, but also, with a few exceptions, in the elements of the secondary subgroups. A similar decrease in the atomic radii occurs in the lanthanides (lanthanide contraction).

This phenomenon has a very important consequence. As a result of lanthanide contraction, the dimensions of the atoms and ions of the elements of the sixth period immediately following the lanthanides (Hf, Ta, W, etc.) are very close to the dimensions of the atoms and ions of the relevant fifth-period elements (Zr, Nb, Mo, etc.). At the same time, for the elements of the fourth and fifth periods, these characteristics appreciably differ (Table 15).

Since the atoms and ions of similar elements of the secondary subgroups of the fifth and sixth periods have not only a similar electron configuration, but also virtually coinciding dimensions, there is much closer similarity in their chemical properties than is observed for the elements of the fourth and fifth periods. For instance, zirconium is considerably closer in its properties to hafnium than to titanium, niobium is similar to tantalum to a greater extent than to vanadium, and so on.

Table 15

Atomic Radii (in nm) of Selected Elements of Secondary Subgroups

Periods	Groups							
	IV	V	VI	VII	VIII		I	
IV	Ti 0.146	V 0.134	Cr 0.127	Mn 0.130	Fe 0.126	Co 0.125	Ni 0.124	Cu 0.128
V	Zr 0.160	Nb 0.145	Mo 0.139	Tc 0.136	Ru 0.134	Rh 0.134	Pd 0.137	Ag 0.144
VI	Hf 0.159	Ta 0.146	W 0.140	Re 0.137	Os 0.135	Ir 0.135	Pt 0.138	Au 0.144

In the free state, the lanthanides are typical metals similar to lanthanum or yttrium. Their oxides are insoluble in water, but readily attach water to form hydroxides. The latter are only sparingly soluble in water and have a basic nature. The salts of the lanthanides as regards their solubility are similar to the relevant salts of lanthanum or yttrium.

Promethium has no stable isotopes and has not been discovered in nature.

Owing to the very great similarity in the chemical properties of lanthanide compounds, it is very difficult to separate these elements in the pure state from their natural compounds. Only in the last 20 or 30 years have effective methods of separating the lanthanides been developed. At present, they have all been obtained in the form of the pure metals.

Many lanthanides and their compounds have found application in various branches of science and engineering. They are used in the production of steel, iron, and non-ferrous metal alloys. Here **misch metal**—an alloy of lanthanides with a predominating content of cerium and lanthanum—is the greatest favourite. The addition of small amounts of rare-earth metals improves the quality of stainless, high-speed, and heat-resistant steels and iron. When 0.35% of misch metal is introduced into nichrome, its service life at 1000 °C grows ten times. The addition of lanthanides to alloys of aluminium and magnesium improves their strength at elevated temperatures.

One of the main consumers of the rare-earth metals is the glass industry. Glass containing cerium does not tarnish under the action of radioactive radiation and is employed in atomic engineering.

Many optical glasses contain lanthanum and neodymium oxides. Small additions of lanthanide oxides are used for decolourizing glasses and for colouring them. For instance, Nd_2O_3 colours glass bright red, and Pr_2O_3 —green. Lanthanide oxides are also used to colour porcelain, glazes, and enamels.

The radioactive isotope of thulium ^{170}Tm is employed to manufacture portable X-ray generators for medical use.

108. Actinides

The actinide family includes 14 *f* elements following actinium in the periodic table:

90 Thorium Th ... 5f ¹⁰ 6s ² 6p ⁶ 6d ² 7s ²	91 Protactinium Pa ... 5f ² 6s ² 6p ⁶ 6d ¹ 7s ²	92 Uranium U ... 5f ³ 6s ² 6p ⁶ 6d ¹ 7s ²	93 Neptunium Np ... 5f ⁴ 6s ² 6p ⁶ 6d ¹ 7s ²
94 Plutonium Pu ... 5f ⁶ 6s ² 6p ⁶ 7s ²	95 Americium Am ... 5f ⁷ 6s ² 6p ⁶ 7s ²	96 Curium Cm ... 5f ⁷ 6s ² 6p ⁶ 6d ¹ 7s ²	97 Berkelium Bk ... 5f ⁹ 6s ² 6p ⁶ 6d ¹ 7s ²
98 Californium Cf ... 5f ¹⁰ 6s ² 6p ⁶ 7s ²	99 Einsteinium Es ... 5f ¹¹ 6s ² 6p ⁶ 7s ²	100 Fermium Fm ... 5f ¹² 6s ² 6p ⁶ 7s ²	101 Mendelevium Md ... 5f ¹³ 6s ² 6p ⁶ 7s ²
102 (Nobelium) (No) ... 5f ¹⁴ 6s ² 6p ⁶ 7s ²		103 (Lawrencium) (Lr) ... 5f ¹⁴ 6s ² 6p ⁶ 6d ¹ 7s ¹	

As in the lanthanides, in the elements of the actinide family, filling of the third electron layer (the sublevel 5f) from the outer one occurs. The configuration of the outer and, as a rule, of the preceding electron layers remains unchanged. This explains the closeness of the chemical properties of the actinides. The difference between the energy states of the electrons occupying the 5f and 6d sublevels in actinide atoms, however, is even smaller than the relevant energy difference in lanthanide atoms. Therefore, in the first members of the actinide family, the 5f electrons readily pass over to the 6d sublevel and can participate in the formation of chemical bonds. As a result, from thorium to uranium, the most characteristic oxidation state of the elements grows from +4 to +6. Further along the actinide series, energy stabilization of the 5f state takes place, while excitation of electrons to the 6d sublevel requires a greater expenditure of energy. As a result, when going from uranium to curium, the most characteristic oxidation state of the elements lowers from +6 to +3 (although compounds with

an oxidation state of +6 and +7 have been obtained for neptunium and plutonium). Berkelium and the elements following it are in the +3 oxidation state in all their compounds.

All the actinides are radioactive. Thorium, protactinium, and uranium are encountered in nature because they have isotopes with great half-lives. Neptunium and plutonium are encountered in nature in negligible amounts. The remaining actinides have been prepared artificially during the last 30 years (see Vol. 1, Sec. 37).

Notwithstanding the instability of actinide atoms, the first seven elements of this family are produced in considerable amounts in the free state and as various compounds such as oxides and halides.

Actinide hydroxides $E(OH)_3$ are basic. The salts corresponding to them resemble the relevant lanthanide salts in their solubility.

The thorium content in the Earth's crust is about $10^{-3}\%$ (mass). Its minerals always accompany the rare-earth elements, uranium, or some other metals. The most important industrial source of thorium is the mineral monazite.

In the free state, thorium is a silvery white refractory plastic metal. The oxidation state of thorium in its compounds is usually +4, its most important oxide is ThO_2 .

Thorium is used in nuclear engineering. The action of neutrons causes natural thorium, which consists almost entirely of the isotope ^{232}Th , to transform into the uranium isotope ^{235}U used as nuclear fuel (see Vol. 1, p. 118). Thorium is also used as a component in a number of alloys. Particularly, magnesium-based alloys containing thorium, zinc, zirconium, and manganese, are distinguished by their low density, high strength, and chemical stability at elevated temperatures.

Uranium was discovered in 1789, but it was separated in the free state (a metal of a gray-steel colour) only in 1841. Its content in the Earth's crust is assessed at $3 \times 10^{-4}\%$ (mass), which corresponds to a total amount of the metal equal to 1.3×10^{14} tonnes. A variety of uranium compounds are found in nature. The most important minerals are uraninite (uranium dioxide UO_2), pitch blende (a phase of varying composition $UO_{2.0-2.6}$), and carnotite [potassium uranyl vanadate $K_2(UO_2)_2 \cdot (VO_4)_2 \cdot nH_2O$]. Uranium ores generally contain not over 0.5% of the useful mineral.

Natural uranium consists of three radioactive isotopes: ^{238}U (about 99.3%), ^{235}U (about 0.7%), and ^{234}U (about 0.005%). Their half-lives are 4.5×10^9 years, 7×10^8 years, and 2.5×10^5 years, respectively.

A very important property of uranium is that the nuclei of some of its isotopes are capable of fission when they capture neutrons; this is attended by the liberation of an enormous amount of energy. This property of uranium is employed in nuclear reactors used as sources of energy, and also underlies the functioning of an atomic

bomb (see Vol. 1, Sec. 37). The isotopes ^{235}U and ^{233}U are used directly for producing nuclear energy. The former is used as natural uranium enriched with this isotope. The most important method of enrichment (or separation of the isotope) is based on the difference in the rate of diffusion of gaseous compounds of the isotopes through porous partitions. Uranium hexafluoride UF_6 (with a sublimation point of 56.5°C) is used as the gaseous compound. The plutonium isotope ^{239}Pu , which can also be used in nuclear reactors and in an atomic bomb, is obtained from the isotope ^{238}U .

Uranium forms quite a large number of compounds. The most typical of them are the compounds of uranium(VI).

Uranium trioxide, or uranic anhydride, UO_3 (an orange powder) is an amphoteric oxide. When it is dissolved in acids, salts are formed (for instance UO_2Cl_2) in which the ion UO_2^{2+} called uranyl is the cation.

Uranyl salts are usually coloured yellowish green and dissolve well in water. The reaction of alkalis with solutions of uranyl salts yields salts of uranic acid H_2UO_4 called uranates, and of diuranic acid $\text{H}_2\text{U}_2\text{O}_7$ called diuranates, for example, sodium uranate Na_2UO_4 and sodium diuranate $\text{Na}_2\text{U}_2\text{O}_7$. The latter salt is used in the production of uranium glass fluorescing with yellowish green light.

SECONDARY SUBGROUPS OF GROUPS IV, V, VI, AND VII

We have already acquainted ourselves with the properties of the elements belonging to the secondary subgroups of the first three groups of the periodic table, and now, before dealing with the remaining secondary subgroups, we can give a general characteristic of the elements forming the secondary subgroups and known as the transition elements.

109. General Characteristic of the Transition Elements

The features of the transition elements are determined first of all by the electron configuration of their atoms whose outer electron layer contains, as a rule, two *s* electrons (sometimes one *s* electron*). The low ionization energies of these atoms are an indication of the comparatively weak bonding of the outer electrons to the nucleus; for instance, for vanadium, chromium, manganese, iron, and cobalt, the ionization energy is 6.74, 6.76, 7.43, 7.90, and 7.86 eV, respectively. It is exactly for this reason that the transition elements have a positive oxidation state in their compounds and play the role of characteristic metals, thus displaying similarity with the metals of the main subgroups.

But there are also substantial distinctions between the metals of the main and secondary subgroups. They are also associated with the features of the electron configuration of the transition elements, namely, with the next-to-last electron layer of their atoms having a *d* sublevel not completely filled by electrons. Atoms of the transition elements can use not only the outer electron layer to form chemical bonds (as in elements of the main subgroups), but also the *d* electrons and the free *d* orbitals of the preceding layer. Consequently, the transition elements are characterized by a variable valence to a much greater extent than the main sub-

* An exception is palladium: its unexcited atom has no *6s* electrons.

group metals. The possibility of creating chemical bonds with the participation of the d electrons and free d orbitals also underlies the strongly expressed ability of the transition elements to form stable complex compounds. As indicated on page 267, the characteristic colour of many transition element compounds is also associated with this circumstance, while the compounds of the main subgroup metals are colourless in the majority of cases.

Almost all the elements of the main subgroups of Groups IV-VII are non-metals, whereas the elements of the secondary subgroups are metals. Therefore, in the right-hand part of the periodic table, the differences in the properties of the elements of the main and secondary subgroups manifest themselves especially strongly. When elements of the main and secondary subgroups are in the higher oxidation state, however, their analogous compounds exhibit an appreciable similarity. For instance, chromium, which is in the secondary subgroup of Group VI, forms the acid oxide CrO_3 , which is close in its properties to sulphur trioxide SO_3 . Both these substances are solid in ordinary conditions and form an acid of the composition H_2EO_4 when they react with water. In exactly the same way, the oxides of manganese and chlorine corresponding to the highest oxidation state of these elements— Mn_2O_7 and Cl_2O_7 —have similar properties and are anhydrides of strong acids corresponding to the general formula HEO_4 .

The explanation of this closeness in properties is that in the highest oxidation state, atoms of elements of the main and secondary subgroups acquire a similar electron configuration. For instance, the chromium atom has the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$. When chromium is in the +6 oxidation state (for example, in the oxide CrO_3), six electrons of its atom (five $3d$ and one $4s$ electrons) together with the valence electrons of adjacent atoms (for CrO_3 —oxygen atoms) form shared electron pairs producing chemical bonds. The remaining electrons not participating directly in the formation of bonds have the configuration $1s^2 2s^2 2p^6 3s^2 3p^6$ corresponding to that of a noble gas. Similarly, in a sulphur atom in the +6 oxidation state (for example, in sulphur trioxide SO_3), six electrons participate in the formation of covalent bonds, and the configuration of the other ones ($1s^2 2s^2 2p^6$) also corresponds to that of a noble gas.

We know that within one period the number of electrons in the outer electron layer of atoms of the main subgroup elements, i.e. s and p elements, grows with their increasing atomic number, the result being a quite rapid transition from typical metals to typical non-metals. In the transition elements, the increase in the atomic number is not attended by an appreciable change in the configuration of the outer electron layer. Consequently, the chemical properties of these elements change in the period, although regularly, but much less sharply than in main subgroup elements.

Within one decade of the transition elements (for example, from scandium to zinc), the maximum stable oxidation state of the elements first grows (owing to the increase in the number of *d* electrons capable of participating in the formation of chemical bonds), and then diminishes (owing to the growth in the interaction of the *d* electrons with the nucleus as its charge becomes greater). For instance, the maximum oxidation state of scandium, titanium, vanadium, chromium, and manganese coincides with the group number, whereas for iron it is six, for cobalt, nickel, and copper—three, and for zinc—two. The stability of compounds corresponding to a definite oxidation state of an element changes accordingly. For example, the oxides TiO and VO containing titanium and vanadium in the oxidation state $+2$ are strong reducing agents, while the similar oxides of copper and zinc (CuO and ZnO) exhibit no reducing properties.

In the main subgroups, the stability of the compounds in which an element exhibits its maximum oxidation state diminishes, as a rule, with an increasing atomic number of the element. For instance, compounds in which the oxidation state of carbon or silicon is $+4$ are quite stable, whereas similar compounds of lead (for example, PbO_2) have a low stability and are readily reduced. The reverse regularity is observed in the secondary subgroups: a growth in the atomic number of an element is attended by an increase in the stability of its compounds in the maximum oxidation states. For instance, the compounds of chromium(VI) are strong oxidizing agents, whereas molybdenum(VI) and tungsten(VI) compounds are not.

Within each secondary subgroup, a substantial similarity is noted in the properties of the elements of the fifth and sixth periods. As indicated in Sec. 107, this is associated with the phenomenon of lanthanide contraction.

TITANIUM SUBGROUP

The titanium subgroup includes the elements of the secondary subgroup of Group IV—titanium, zirconium, hafnium, and the artificially obtained (see Vol. 1, p. 117) kurchatovium. These elements display stronger metallic properties than the metals of the main subgroup of Group IV—tin and lead. An atom of a titanium subgroup element has two electrons in its outer layer, and 10 electrons in the preceding layer, of which two are in the *d* sublevel. For this reason, the most characteristic oxidation state of the titanium subgroup metals is $+4$.

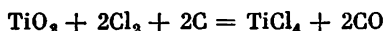
In the free state, titanium and its analogues are typical metals similar to steel in appearance. They are all refractory and stable with respect to air and water.

110. Titanium

Titanium is very abundant in nature. Its content in the Earth's crust is 0.6% (mass), i.e. higher than the content of metals widely used in engineering such as copper, lead, and zinc.

Minerals containing titanium occur everywhere in nature. The most important of them are titanomagnetites $\text{FeTiO}_3 \cdot n\text{Fe}_3\text{O}_4$, ilmenite FeTiO_3 , sphene or titanite CaTiSiO_5 , and rutile TiO_2 . In the USSR, titanium ore deposits occur in the Urals.

In the industrial production of titanium, the ore or concentrate is converted into titanium dioxide TiO_2 , which is then chlorinated. But even at 800 to 1000 °C, chlorination proceeds slowly. Its rate is sufficient for practical purposes in the presence of carbon, which chiefly combines with the oxygen to form CO:



The titanium(IV) chloride obtained is reduced with magnesium:



and the mixture formed is heated in a vacuum. The magnesium and its chloride evaporate and are deposited in a condenser. The residue—spongy titanium—is remelted to produce a compact ductile metal.

Admixtures of oxygen, nitrogen, and carbon greatly detract from the mechanical properties of titanium, and in a large amount convert it into a brittle material unsuitable for practical use. Since titanium reacts with these non-metals at elevated temperatures, its reduction is conducted in a sealed apparatus in an atmosphere of argon, and its purification and remelting—in a high vacuum.

The iodide method (see Sec. 79) is used to produce small amounts of highly pure titanium.

Metallic titanium melts at 1665 °C; its density is 4.505 g/cm³. Titanium is a moderately active metal. The standard electrode potential of the system Ti/Ti^{2+} is -1.63 V. But owing to the formation of a dense protective film on the surface of the metal, titanium has an exceedingly high resistance to corrosion superior to that of stainless steel. It does not oxidize in air, in sea water, and does not change in a number of aggressive chemical media, particularly in dilute and concentrated nitric acid and even in aqua regia.

Its very high resistance to corrosion makes titanium an excellent material for manufacturing chemical equipment. But the main property of titanium that facilitates its constantly growing use in modern engineering is the high heat resistance of both titanium itself and its alloys with aluminium and other metals. These alloys also retain their strength and other high mechanical properties at elevated temperatures. All this makes titanium alloys very valuable materials for aircraft and rocket engineering.

Titanium is only slightly heavier than aluminium, but is three times stronger. This opens up broad prospects for the use of titanium in various fields of mechanical engineering. It is sufficient to note that the use of components made from titanium and its alloys in internal-combustion engines allows the mass of these engines to be lowered by about 30%.

The extensive possibilities of using titanium in engineering have resulted in the tremendous growth of its production. In 1948, the first 2.5 tonnes of commercial titanium were produced, in 1954 the world production of this metal was 7000 tonnes, and in 1957 it reached 30 000 tonnes. Such rates of growth were never observed in the production of any other metal.

At an elevated temperature, titanium combines with the halogens, oxygen, sulphur, nitrogen, and other elements. This underlies the use of alloys of titanium with iron (**ferrotitanium**) as an addition to steel. The titanium combines with the nitrogen and oxygen in the molten steel and thus prevents liberation of the latter when the steel solidifies—homogeneous castings containing no voids are obtained.

Titanium combines with carbon to form a carbide. Alloys whose hardness approaches that of diamond are produced from titanium and tungsten carbides with the addition of cobalt.

Titanium dioxide TiO_2 is a white refractory substance insoluble in water and dilute acids. It is an amphoteric oxide, but both its basic and acid properties are weak.

Titanium dioxide is used in the manufacture of refractory glasses, glazes, enamels, heat-resistant laboratory utensils, and also in the preparation of white oil paint having a high covering power (titanium white).

The fusion of TiO_2 with BaCO_3 yields **barium titanate** BaTiO_3 . This salt has a very high permittivity and, in addition, can deform under the action of an electric field. Barium titanate crystals are used in high-capacity electrical capacitors of a small size, in ultrasonic apparatus, sound pickups, and hydroacoustical equipment.

111. Zirconium. Hafnium

Zirconium is a quite abundant element: its content in the Earth's crust is 0.025% (mass). Zirconium is very dispersed, however, and more or less considerable accumulations of it are rare.

In the free state, zirconium is a lustrous metal with a density of 6.45 g/cm^3 and a melting point of 1855°C . Zirconium containing no impurities is very plastic and readily lends itself to cold and hot working. Like titanium, the mechanical properties of zirconium sharply deteriorate when it contains admixtures of non-metals, especially oxygen.

One of the most valuable properties of metallic zirconium is its high resistance to corrosion in various media. For instance, it does not dissolve in hydrochloric and nitric acids, and in alkalis.

Zirconium does not virtually capture slow (thermal) neutrons. This property combined with its high resistance to corrosion and high mechanical strength at elevated temperatures places zirconium and its alloys among the principal structural materials for power atomic reactors. The most important zirconium alloys include **zircalloys**—alloys containing small amounts of tin, iron, chromium, and nickel.

In the production of steel, additions of zirconium remove oxygen, nitrogen, and sulphur from it. Zirconium is also used as an alloying component in some armour, stainless, and heat-resistant steels.

The addition of zirconium to copper considerably improves its strength without virtually affecting its high electrical conductance. A magnesium-based alloy with the addition of 4 to 5% of zinc and 0.6 to 0.7% of zirconium is twice as hard as pure magnesium and does not lose its strength at 200 °C. The quality of aluminium alloys also considerably improves when zirconium is added to them.

Zirconium dioxide ZrO_2 has a high melting point (about 2700 °C), an extremely low coefficient of thermal expansion, and stability to chemical action. It is used to manufacture a variety of refractory articles, for example, crucibles. In the glass industry, ZrO_2 is employed to produce refractory glasses, and in the ceramic industry to produce enamels and glazes.

Zirconium carbide ZrC owing to its great hardness is used as a grinding material and as a substitute for diamonds in cutting glass.

Hafnium has no minerals of its own and usually accompanies zirconium in nature. It is quite similar to zirconium in its chemical properties, but differs from it in its ability to intensively capture electrons, which explains the use of this element in the controlling and protective devices of atomic reactors. Both metallic hafnium and some of its compounds such as hafnium dioxide HfO_2 are used for this purpose; the dioxide is also employed in the production of optical glasses with a high refractive index.

VANADIUM SUBGROUP

The vanadium subgroup includes the elements of the secondary subgroup of Group V: **vanadium**, **niobium**, and **tantalum**. Having in the outer electron layer of an atom two or one electron, these elements differ from those of the main subgroup (nitrogen, phosphorus, etc.) in the predomination of metallic properties and the absence of hydrogen compounds. But the derivatives of the elements

of both subgroups have substantial resemblance in their maximum oxidation state.

The most typical compounds of vanadium and its analogues are those in which their oxidation state is +5. Their higher oxides display the properties of acid oxides and form vanadic, niobic, and tantalic acids, respectively. A number of salts correspond to these acids. The lower oxides have basic properties.

In the free state, vanadium, niobium, and tantalum are quite stable to chemical action and have high melting points. These metals as well as chromium, molybdenum, tungsten, and rhenium (see Secs. 114-118), and also ruthenium, rhodium, osmium, and iridium (see Table 18, p. 372) belong to the **refractory metals**. It is customary practice to call metals refractory when their melting point exceeds that of chromium (1890 °C).

The refractory metals in the pure state and as alloys have acquired an exclusive significance lately in a number of branches of industry involving new techniques and equipment.

112. Vanadium

Vanadium compounds are distributed widely in nature, but they are very dispersed and form no more or less considerable accumulations. The total vanadium content in the Earth's crust is assessed at 0.0015% (mass).

The main sources of vanadium in the USSR are iron and complex ores containing small amounts of vanadium. Generally, what is produced from the ores is either an alloy of vanadium with iron known as **ferrovanadium**, or vanadium anhydride V_2O_5 . The pure metal is produced from its compounds: by the calcium-thermic reduction of V_2O_5 , the magnesium-thermic reduction of VCl_3 , or the thermal dissociation of VI_2 .

Pure vanadium is a silvery ductile metal with a density of 5.96 g/cm³ that melts at about 1900 °C. Like titanium, the mechanical properties of vanadium sharply deteriorate when it contains admixtures of oxygen, nitrogen, and hydrogen.

Vanadium is distinguished by its high chemical stability in water, sea water, and in alkali solutions. It dissolves in hydrofluoric acid, in concentrated nitric and sulphuric acids, and in aqua regia.

Vanadium finds its main application as an addition to steels. Steel containing only from 0.1 to 0.3% of vanadium is very strong, elastic, and is not sensitive to jolts and impacts, which is especially important, for example, for motor vehicle axles, constantly experiencing shocks. As a rule, vanadium is introduced into steel in combination with other alloying elements: chromium, nickel, tungsten, and molybdenum. Vanadium is used to the greatest extent in the

production of tool and structural steels (see Sec. 127). It is also employed for alloying iron.

Vanadium forms four oxides: VO , V_2O_3 , VO_2 , and V_2O_5 . The higher oxide V_2O_5 has a clearly expressed acid nature, the dioxide VO_2 is amphoteric, while both lower oxides exhibit only basic properties. Of the greatest significance is V_2O_5 and its derivatives.

Vanadium(V) oxide, or vanadic anhydride V_2O_5 is an orange substance readily dissolving in alkalis to form salts of metavanadic acid HVO_3 called vanadates.

Vanadium(V) oxide and vanadates are used in the chemical industry as catalysts in the contact process of producing sulphuric acid and in some organic syntheses. Vanadium compounds are also employed in the glass industry, in medicine, and in photography.

113. Niobium. Tantalum

The content of niobium in the Earth's crust is 0.002, and of tantalum 0.0002% (mass). The two elements have much in common with vanadium. In the free state they are refractory metals, hard, but not brittle, and well lending themselves to mechanical working. The density of niobium is 8.57 g/cm^3 , and of tantalum is 16.6 g/cm^3 . Their melting points are 2500 and 3000 °C, respectively.

Both metals, especially tantalum, are stable in many aggressive media. They do not react with hydrochloric, sulphuric, nitric, and chloric acids, and with aqua regia because a thin, but very strong and chemically stable oxide film forms on the surface of these metals. On tantalum, for instance, the film is tantalum(V) oxide Ta_2O_5 . This is why tantalum reacts only with substances like fluorine, hydrogen fluoride, hydrofluoric acid, and melts of alkalis that can react with the oxide film or penetrate through it.

Niobium is one of the chief components of many heat-resistant and corrosion-resistant alloys. Of especially great importance are the heat-resistant alloys of niobium that are employed in the production of gas turbines, jet engines, and rockets. Niobium is also introduced into stainless steels. It sharply improves their mechanical properties and resistance to corrosion. Steels containing from 1 to 4% of niobium are highly heat-resistant and are used to manufacture high-pressure boilers. Steel with an addition of niobium is a superb material for the electrical welding of steel structural members: its use ensures an unusually high strength of the welds.

The most important spheres of application of tantalum are electronics and mechanical engineering. In electronics, it is used for making electrolytic capacitors, the anodes of powerful tubes, and grids. In chemical engineering, it is used to make the components of equipment employed in the production of acids. Metals such as

rare-earth ones are melted in tantalum crucibles. It goes to make the heaters of high-temperature furnaces. Tantalum does not react with the living tissues of the human organism and does not harm them. This is why it is employed in surgery for joining broken bones.

In many spheres of application of tantalum, its alloys with niobium compete with it. This produces a great economical effect because niobium is cheaper than tantalum.

Niobium and tantalum carbides are extremely hard and are used in the metal-working industry for manufacturing cutting tools.

CHROMIUM SUBGROUP

This subgroup is formed by the metals of the secondary subgroup of Group VI—chromium, molybdenum, and tungsten.

The outer electron layer of an atom of the chromium subgroup elements contains one or two electrons, which explains the metallic nature of these elements and their difference from the elements of the main subgroup. At the same time, their maximum oxidation state is +6 because, apart from the outer electrons, the corresponding number of electrons from the incompletely built up next-to-last layer can participate in bond formation.

The most typical derivatives of chromium and its analogues are those of the maximum oxidation state. They are similar in many respects to the relevant sulphur compounds.

114. Chromium

The amount of chromium in the Earth's crust is 0.02% (mass). It occurs in nature chiefly as chromite $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, rich deposits of which are in Kazakhstan and the Urals.

When chromite is reduced with coal, the product is an alloy of chromium with iron—ferrochrome, which is used directly in the iron and steel industry in the production of chromium steels. To produce pure chromium, first chromium(III) oxide is prepared, and it is then reduced by the aluminothermic method.

Chromium is a hard lustrous metal melting at 1890 °C; its density is 7.19 g/cm³. At room temperature, chromium is indifferent to water and air. Dilute sulphuric and hydrochloric acids dissolve chromium with the liberation of hydrogen. Chromium does not dissolve in cold concentrated nitric acid and becomes passive after being treated with it.

Metallic chromium is used for chromium plating, and also as one of the most important components of alloyed steels. The introduction of chromium into steel improves its resistance to corrosion

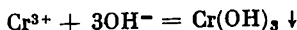
both in aqueous media at ordinary temperatures, and in gases at elevated temperatures. Chromium steels also have an increased hardness. Chromium is a component of stainless, acid-resistant, and heat-resistant steels (see also p. 224, and Sec. 127).

Chromium forms three oxides: **chromium(II) oxide** CrO having a basic nature, **chromium(III) oxide** Cr_2O_3 exhibiting amphoteric properties, and **chromium(VI) oxide** or **chromic anhydride** CrO_3 —an acid oxide. Three series of chromium compounds are known corresponding to these three oxides.

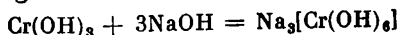
Chromium(II) Compounds. When chromium is dissolved in hydrochloric acid, a blue solution is obtained containing **chromium(II) chloride** CrCl_2 . If an alkali is added to this solution, a yellow precipitate of **chromium(II) hydroxide** Cr(OH)_2 is formed. The compounds of chromium(II) are not stable and are rapidly oxidized by the oxygen of the air to chromium(III) compounds.

Chromium(III) Compounds. *Chromium(III) oxide* Cr_2O_3 is a green refractory substance used under the name of **chrome green** to prepare distemper and oil paints. When fused with silicates, chromium(III) oxide colours them green and is therefore used for colouring glass and porcelain. This oxide is also a component of polishing compounds.

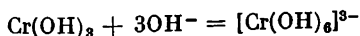
Chromium(III) hydroxide Cr(OH)_3 forms a bluish gray precipitate when alkalis react with a chromium(III) salt:



Like aluminium and zinc hydroxides, it is amphoteric and dissolves in acids to form chromium(III) salts, and in alkalis to form emerald green solutions of **chromites**, for instance:



or



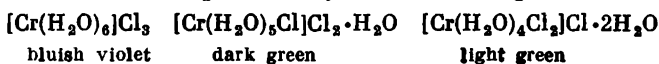
Chromites prepared by fusing Cr_2O_3 with oxides of other metals and known chiefly for divalent metals have a composition corresponding to the formula $\text{M(CrO}_2)_2$ and are salts of **metachromous acid** HCrO_2 . They include the natural chromite $\text{Fe(CrO}_2)_2$.

The most widespread of the chromium(III) salts is the double salt of chromium and potassium—**chrome alum** $\text{KCr(SO}_4)_2 \cdot 12\text{H}_2\text{O}$ that forms bluish violet crystals. Chrome alum is used in the leather industry for tanning hides and in the textile industry as a mordant in dyeing.

Chromium(III) salts resemble aluminium salts in many features. They become greatly hydrolyzed in aqueous solutions and readily transform into the basic salts. Chromium(III), like aluminium, forms no salts with weak acids.

Solutions of chromium(III) salts generally have a bluish violet colour, but turn green when heated. In a certain time after being

cooled, they again acquire their previous colour. This colour change is explained by the formation of isomeric salt hydrates that are complex compounds in which all or part of the water molecules are coordinationally bonded in the inner sphere of the complex. In some cases, such hydrates were successfully separated in the solid state. For instance, the crystal hydrate of chromium(III) chloride $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is known in three isomeric forms—bluish violet, dark green, and light green crystals having an identical composition. The structure of these isomers can be established on the basis of the different reaction of the freshly prepared solutions with silver nitrate. When the latter reacts with a solution of the bluish violet hydrate, all the chlorine precipitates; two-thirds of the chlorine precipitate from a solution of the dark green hydrate, and only one-third from a solution of the light green hydrate. Taking into account these data, and also the coordination number of chromium equal to six, the structure of the crystal hydrates being considered can be expressed by the following formulas:

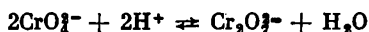


Hence, the isomerism of the chromium(III) chloride hydrates is due to the different distribution of the same groups (H_2O and Cl^-) between the inner and outer coordination spheres and can be an example of hydrate isomerism (p. 262).

Chromium(VI) Compounds. The most important chromium(VI) compounds are chromium trioxide, or chromic anhydride CrO_3 , and the salts of the relevant acids—chromic H_2CrO_4 and dichromic $\text{H}_2\text{Cr}_2\text{O}_7$. Both acids exist only in an aqueous solution and upon attempts to separate them from the solution they decompose into chromium trioxide and water. Their salts, however, are quite stable. The salts of chromic acid are called **chromates**, and of dichromic acid—**dichromates** or **bichromates**.

Almost all chromates are yellow. Some of them are used as pigments. For instance, lead chromate PbCrO_4 , which is insoluble in water, is used under the name of chrome yellow for preparing yellow oil paint.

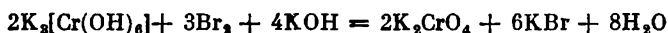
If a solution of a chromate, for example potassium chromate K_2CrO_4 , is acidified, the purely yellow colour of the solution changes to an orange one owing to the transformation of the CrO_4^{2-} ions into $\text{Cr}_2\text{O}_7^{2-}$ ones. A salt of dichromic acid—potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ —can be separated from the solution as orange-red crystals. The reaction of transformation of a chromate into a dichromate is as follows:



The reaction is reversible. This signifies that when a dichromate is dissolved in water, there is always formed a certain, though

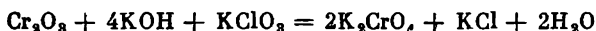
insignificant, amount of H^+ and CrO_4^{2-} ions. This is why a dichromate solution has an acid reaction. If an alkali is added to a dichromate solution, the hydroxide ions will bind the hydrogen ions in the solution, equilibrium will shift to the left, and as a result the dichromate will transform into a chromate. Hence, in the presence of excess hydroxide ions, a solution virtually contains only CrO_4^{2-} ions, i.e. a chromate, and in the presence of excess hydrogen ions—only $Cr_2O_7^{2-}$ ions, i.e. a dichromate.

Alkali metal chromates are prepared by acidifying chromium(III) compounds in the presence of an alkali. For instance, when bromine reacts with a potassium chromite solution, potassium chromate is formed:



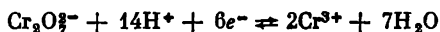
That oxidation occurs can be seen from the fact that the emerald green colour of the chromite solution turns into a bright yellow one.

Chromates can also be prepared by fusing Cr_2O_3 with an alkali in the presence of an oxidizing agent, for instance potassium chlorate:



Chromates and dichromates are strong oxidizing agents and are widely used for oxidizing various substances. Oxidation is conducted in an acid solution and is usually attended by a sharp change in colour [dichromates are orange, while chromium(III) salts are green or greenish violet].

We have seen that chromium(III) and chromium(VI) compounds exist in different forms in acid and in alkaline solutions: as the Cr^{3+} or $Cr_2O_7^{2-}$ ions in an acid solution, and as the $[Cr(OH)_6]^{3-}$ or CrO_4^{2-} ions in an alkaline solution. Consequently, the mutual transformation of chromium(III) and chromium(VI) compounds proceeds differently depending on the reaction of a solution. The equilibrium that sets in in an acid solution is



and in an alkaline one



Both in an acid and an alkaline solution, however, oxidation of chromium(III) results in diminishing of the pH of the solution. The reverse process—reduction of chromium(VI)—is attended by an increase in the pH. Hence, in accordance with Le Chatelier's principle, when the acidity of a solution grows, equilibrium shifts in the direction of the reduction of chromium(VI), and when the acidity diminishes, in the direction of oxidation of chromium(III). In other words, the oxidizing properties of chromium(VI) compounds

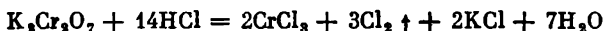
are expressed the greatest in an acid solution, and the reducing properties of chromium(III) compounds—in an alkaline one. It is exactly for this reason, as indicated above, that chromites and chromates are oxidized in the presence of an alkali, while chromium(VI) compounds are used as oxidizing agents in acid solutions.

A few examples of oxidation-reduction reactions proceeding with the participation of dichromates are given below.

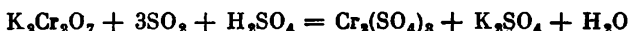
1. When hydrogen sulphide is passed through a dichromate solution acidified with sulphuric acid, the orange colour of the solution turns green, and the liquid simultaneously becomes turbid owing to the liberation of sulphur:



2. When concentrated hydrochloric acid reacts with potassium dichromate, chlorine is liberated and a green solution is obtained that contains chromium(III) chloride:



3. If sulphur dioxide is passed through a concentrated solution of potassium dichromate containing a sufficient amount of sulphuric acid, equimolecular amounts of potassium and chromium(III) sulphates are formed:

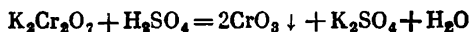


When the solution is evaporated, chrome alum $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ separates from it. This reaction is employed for producing chrome alum commercially.

The most important dichromates are potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ and sodium dichromate $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ that form orange-red crystals. Both salts are widely used as oxidizing agents in the production of many organic compounds, in the leather industry in tanning hides, and in the match and textile industries. A mixture of concentrated sulphuric acid with an aqueous solution of potassium or sodium dichromate known as **chromic acid mixture** is often used for vigorous oxidation and for cleaning chemical utensils.

All salts of chromic acids are poisonous.

Chromium trioxide, or **chromic anhydride** CrO_3 , precipitates as dark red needle-like crystals when concentrated sulphuric acid is reacted with a saturated solution of potassium or sodium dichromate:



Chromium trioxide is one of the strongest oxidizing agents. For example, ethyl alcohol ignites when it comes into contact with it. Upon oxidizing a substance, chromium trioxide transforms into chromium(III) oxide Cr_2O_3 .

Chromium trioxide readily dissolves in water to form chromic and dichromic acids.

115. Molybdenum (*Molibdenium*)

The main natural compound of molybdenum is **molybdenite**, or **molybdenum glance** MoS_2 —a mineral greatly resembling graphite and considered as such for a long time. In 1778, Karl Scheele showed that when molybdenite is reacted with nitric acid, a white residue is obtained having the properties of an acid. He called it molybdic acid and concluded that the mineral itself is the sulphide of a new element. Five years later, the element was obtained in the free state by roasting molybdic acid with charcoal.

The total content of molybdenum in the Earth's crust is 0.001% (mass). Deposits of molybdenum ores occur in the USSR, Chile, Mexico, Norway, and Morocco. Large amounts of molybdenum are contained in sulphide copper ores.

To produce metallic molybdenum from molybdenite, the latter is converted by roasting into MoO_3 , from which the metal is reduced with hydrogen. The molybdenum is obtained as a powder.

Compact molybdenum is mainly produced by **powder metallurgy** techniques. This process consists in pressing the powder into a blank and sintering the latter.

The blanks pressed from the powder are bodies of a definite shape, usually bars. Molybdenum bars are produced in steel press moulds at a pressure up to 300 MPa. The bars are sintered in a hydrogen atmosphere in two steps. The first—preliminary sintering—is conducted at 1100-1200 °C and is aimed at increasing the strength and electrical conductance of the bars. The second step—high-temperature sintering—is conducted by passing an electric current through the bars, which gradually heats them to 2200-2400 °C. The product is a compact metal. The sintered bars are delivered for mechanical processing such as forging or drawing.

Large molybdenum blanks—ingots with a mass up to 2000 kg—are produced by **arc melting**. Melting in arc furnaces is conducted in a vacuum. An arc is struck between the cathode (a bundle of sintered molybdenum bars) and the anode (a cooled copper crucible). The metal of the cathode melts and is gathered in the crucible. Owing to the high thermal conductivity of the copper and the rapid removal of heat, the molybdenum solidifies.

To produce highly pure molybdenum and other refractory metals, **electron-beam melting** is used. It is based on the conversion into heat of the major part of the kinetic energy of electrons when they collide with the surface of the metal. An installation for electron-beam melting consists of an electron gun generating a controllable stream of electrons, and a melting chamber. Melting is conducted in a high vacuum, which ensures the removal of the impurities evaporating at the melting point (O, N, P, As, Fe, Cu, Ni, etc.). In addition, a high rarefaction is needed to prevent collisions of

the electrons with molecules of the air, which would result in the electrons losing energy. After electron-beam melting the purity of the molybdenum rises to 99.9%.

Besides compact refractory metals, the powder metallurgy techniques are used to produce a number of other materials. The most important of them are carbide hard alloys, ferrites, porous materials, and cermets.

Carbide hard alloys are treated in the following section, and ferrites in Sec. 128. Articles made from porous materials include porous bearings and metallic filters. The former are manufactured by sintering bronze and graphite powders. The pores of such bearings are impregnated with a lubricant, which allows them to be used in conditions of lubrication and when there is a danger of contaminating products (for example, in the food or textile industries). Metallic filters are made by sintering powders of copper, nickel, and stainless steel. They are used to purify a variety of liquids, oils, liquid fuel, have a prolonged service life, are stable at elevated temperatures, and can be manufactured with a broad range of porosity.

Cermets, or metalloceramic materials, are produced by sintering mixtures of metal powders and non-metallic components—refractory oxides, carbides, borides, etc. Metals of the chromium and iron subgroups are mainly used as the metallic component. These materials combine the refractoriness, hardness, and heat resistance of ceramics with the conductance, plasticity, and other properties of metals.

Molybdenum is a silvery white metal with a density of 10.2 g/cm^3 melting at 2620°C . At room temperature, it does not change in air, but when heated it oxidizes into the white trioxide MoO_3 . Hydrochloric and dilute sulphuric acids do not react with molybdenum at room temperature; it dissolves in nitric acid or in hot concentrated sulphuric acid.

About 80% of all the molybdenum produced goes to make special grades of steel. It is a component of many stainless steels; in addition, its introduction increases their heat resistance.

An alloy of molybdenum with tantalum is used to make laboratory utensils employed in chemical laboratories instead of platinum ones. Pure molybdenum goes to make components of electronic valves and incandescent lamps—anodes, grids, cathodes, current inlets, and filament holders.

Molybdenum exhibits positive oxidation states in its compounds, namely, six, five, four, three, and two. Molybdenum(VI) compounds are most stable. Of the greatest importance among them are salts of molybdic acid H_2MoO_4 (**molybdates**), which often have a complex composition.

Ammonium molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ is used for detecting and quantitatively determining phosphoric acid, with which it

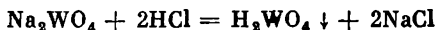
forms a characteristic yellow precipitate of the composition $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 6\text{H}_2\text{O}$. The latter is the ammonium salt of the complex phosphomolybdic acid belonging to the class of heteropoly acids (see p. 259).

116. Tungsten (*Wolfram*)

As regards its occurrence in the Earth's crust [0.007% (mass)], tungsten is inferior to chromium, but is ahead of molybdenum. The natural compounds of tungsten in the majority of cases are tungstates—salts of tungstic acid H_2WO_4 . For instance, the most important tungsten ore—wolframite—consists of iron and manganese tungstates. The mineral scheelite CaWO_4 is also encountered quite frequently.

To extract tungsten from wolframite, the latter is fused with soda in the air. The tungsten transforms into sodium tungstate Na_2WO_4 that is recovered from the melt with water, while the iron and manganese are transformed into the compounds Fe_2O_3 and Mn_3O_4 that are insoluble in water.

The aqueous solution is reacted with hydrochloric acid to separate the free tungstic acid as an amorphous yellow precipitate:



Roasting of tungstic acid transforms it into tungsten trioxide WO_3 . By reducing it with hydrogen or carbon (for which purpose the purest grades of carbon black are used), a powder of metallic tungsten is obtained that is further processed in the same way as molybdenum powder to produce the compact metal.

Tungsten is a heavy white metal with a density of 19.3 g/cm^3 . Its melting point (about 3400°C) is higher than that of all the other metals. Tungsten can be welded and drawn out into thin filaments.

Tungsten oxidizes in air only when red hot. It is very stable with respect to acids, even to aqua regia, but does dissolve in a mixture of nitric acid and hydrogen fluoride.

The major part of the tungsten produced is used in metallurgy for preparing special steels and alloys. High-speed tool steel contains up to 20% of tungsten and has the property of self-hardening. Such steel does not lose its hardness even when red hot. This is why the use of cutters produced from tungsten steel considerably increases metal cutting speeds.

In addition to high-speed steels, other tungsten and chromium-tungsten steels have found broad application. For example, a steel containing from 1 to 6% of tungsten and up to 2% of chromium goes to make saws, milling cutters, punches, and dies.

Being the most refractory metal, tungsten is included in a number of heat-resistant alloys. Particularly, its alloys with cobalt

and chromium—stellites—have a great hardness, wear resistance, and heat resistance. Alloys of tungsten with copper and with silver combine high electrical and thermal conductivity with wear resistance. They are used to make the working parts of knife-blade switches, circuit breakers, and electrodes for spot welding.

Pure tungsten in the form of wire, band, and a variety of components is used in the production of electric lamps, in radio electronics, and X-ray equipment. Tungsten is the best material for the filaments of incandescent lamps: its elevated working temperature (2200-2500 °C) ensures a high luminous efficiency, and its very slight evaporation—a prolonged service life of filaments made from it. Tungsten wire and bars are also used as the heating elements in high-temperature furnaces (up to 3000 °C).

Tungsten carbide WC has a very great hardness (close to that of diamond), wear resistance, and refractoriness. The most productive hard tool alloys have been developed on its basis. They include 85-95% of WC and 5-15% of cobalt imparting the required strength to the alloy. Some grades of such alloys contain titanium, tantalum, and niobium carbides in addition to tungsten carbide. All these alloys are produced by powder metallurgy techniques and are employed chiefly for making the working parts of cutting and boring tools.

Tungsten compounds are very similar to those of molybdenum. The most important of them is tungstic acid H_2WO_4 and its salts.

MANGANESE SUBGROUP

This subgroup includes the elements of the secondary subgroup of Group VII: **manganese, technetium, and rhenium**. The relation between them and the elements of the main subgroup of Group VII—the halogens—is about the same as between the elements of the main and secondary subgroups of Group VI. Having in their outer electron layer only two electrons, manganese and its analogues cannot gain electrons and, unlike the halogens, form no compounds with hydrogen. But the higher oxygen compounds of these elements are to a certain degree similar to the relevant halogen compounds because here also seven electrons can participate in the formation of bonds with oxygen. Therefore, their maximum oxidation state is +7.

Manganese itself is of the greatest practical importance among the elements of the subgroup bearing its name. Rhenium, discovered in 1925, is a rare element, but owing to a number of valuable properties, it has found applications in engineering. Technetium is not encountered in the Earth's crust. It was obtained in 1937 artificially by bombarding nuclei of molybdenum atoms with nuclei of the heavy hydrogen (deuterium) isotope—deuterons (see Vol. 1, p. 116). Technetium was the first element to be obtained artificially, by "technical" means, whence its name.

117. Manganese (*Manganum*)

Manganese is one of the quite abundant elements, forming 0.1% (mass) of the Earth's crust. The most widespread manganese-containing mineral is **pyrolusite**, which is manganese dioxide MnO_2 . The minerals **hausmannite** Mn_3O_4 and **brownite** Mn_2O_3 are also quite important.

The USSR has large deposits of manganese. As regards its reserves of high-grade manganese ores, the USSR occupies the first place in the world.

Manganese is produced either by the electrolysis of an MnSO_4 solution, or by reduction from its oxides with silicon in electric furnaces. The second (silicothermic) method is cheaper, but yields a less pure product. In the electrolytic method, the ore is reduced to manganese compounds with the oxidation state +2. These compounds are next dissolved in a mixture of sulphuric acid and ammonium sulphate. The solution obtained is electrolyzed. The deposited metal is removed from the cathodes and remelted into ingots.

Manganese is a silvery hard brittle metal. Its density is 7.44 g/cm^3 , and its melting point is 1245°C . Four crystalline modifications of manganese are known, each of which is thermodynamically stable within a definite temperature range. Below 707°C , alpha-manganese is stable, and has an intricate structure (its elementary cell includes 58 atoms), which explains its brittleness.

Manganese is between aluminium and zinc in the electromotive series: the standard electrode potential of the system Mn^{2+}/Mn is -1.179 V . In the air, manganese is covered with a thin oxide film preventing its further oxidation even when heated. But in a finely divided state, manganese is oxidized quite readily. Water at room temperature reacts with manganese very slowly, and more rapidly when heated. It dissolves in dilute hydrochloric and nitric acids, and also in hot concentrated sulphuric acid (it is virtually insoluble in cold sulphuric acid), forming Mn^{2+} cations.

Manganese has found its chief use in the production of alloyed steels. Manganese steel containing up to 15% of Mn is very hard and strong. It is used to make the working parts of crushing machines, ball mills, and railway rails. Manganese is also added to a number of magnesium-based alloys, improving their resistance to corrosion. An alloy of copper with manganese and nickel—**manganin** (see Sec. 86) has a low temperature resistance coefficient. Manganese is introduced in small amounts into many aluminium alloys.

Manganese forms four simple oxides (MnO , Mn_2O_3 , MnO_2 , and Mn_2O_7) and the mixed oxide Mn_3O_4 (or $\text{MnO} \cdot \text{Mn}_2\text{O}_3$). The first two oxides have basic properties, manganese dioxide MnO_2 is amphoteric, while the higher oxide Mn_2O_7 is the anhydride of **perman-**

ganic acid HMnO_4 . Derivatives of manganese(VI) are also known but the corresponding oxide MnO_3 has never been obtained.

Compounds of manganese(II)—manganese dioxide, and the salts of permanganic acid (permanganates), in which manganese is in the +7 oxidation state—are the most important compounds from a practical viewpoint.

Manganese(II) Compounds. The salts of manganese(II) are obtained when manganese is dissolved in dilute acids or when acids react with various natural compounds of manganese. For instance, **manganese(II) chloride** MnCl_2 crystallizes as pale pink crystals from the solution remaining after chlorine is prepared by reacting hydrochloric acid with manganese dioxide. Solid manganese(II) salts are usually pink, while their solutions are almost colourless.

When alkalis are reacted with solutions of manganese(II) salts, a white precipitate of **manganese(II) hydroxide** Mn(OH)_2 is formed. The precipitate dissolves readily in acids. It rapidly darkens in air, oxidizing into the brown manganese(IV) hydroxide Mn(OH)_4 .

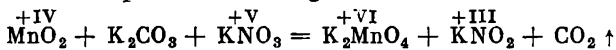
Manganese(II) oxide MnO is obtained as a green powder when higher manganese oxides are reduced with hydrogen.

Manganese(IV) Compounds. The most stable compound of manganese is dark brown **manganese dioxide** MnO_2 ; it readily forms both in oxidation of the lower and in reduction of the higher compounds of manganese. We have already mentioned that MnO_2 is an amphoteric oxide; both its acid and basic properties, however, are very weak.

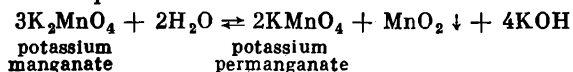
In an acid medium, manganese dioxide is a quite vigorous oxidizing agent. It is used as such in the preparation of chlorine from hydrogen chloride and in dry galvanic cells. Manganese(IV) salts, for example MnCl_4 and $\text{Mn(SO}_4)_2$, are very unstable.

Manganese(VI) and (VII) Compounds. When manganese dioxide is fused with potassium carbonate and nitrate, a green melt is obtained dissolving in water with the formation of a beautiful green solution. Dark green crystals of **potassium manganate** K_2MnO_4 —a salt of **manganic acid** H_2MnO_4 —can be separated from this solution. Potassium manganate is very unstable even in solution.

The reaction of potassium manganate formation is as follows:



If a manganate solution is left standing in the air, its colour gradually changes from green to crimson, and a dark brown precipitate forms. The explanation is that in an aqueous solution, manganates spontaneously transform into salts of permanganic acid HMnO_4 (**permanganates**) with the simultaneous formation of manganese dioxide. The equation of the reaction is:



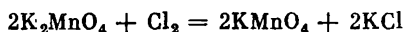
or in the net ionic form:



In this reaction, one MnO_4^{2-} ion oxidizes the other two ions into MnO_4^- ions, being reduced into MnO_2 .

The process of transformation of a manganate into a permanganate is reversible. Consequently, in the presence of an excess of hydroxide ions, a green manganate solution can remain unchanged for a long time. If an acid is added, however, that binds the hydroxide ions, the green colour almost instantaneously changes to crimson.

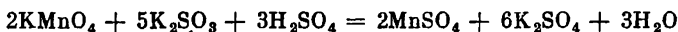
When strong oxidizing agents (for instance chlorine) react with a manganate solution, the latter completely transforms into a permanganate:



Potassium permanganate KMnO_4 is the most broadly used salt of permanganic acid. It crystallizes as beautiful dark violet, almost black prisms moderately soluble in water. Solutions of KMnO_4 have a dark crimson, and in greater concentrations—a violet colour that is a feature of MnO_4^- ions. Like all manganese(VII) compounds, potassium permanganate is a strong oxidizing agent. It readily oxidizes many organic substances, transforms iron(II) salts into iron(III) ones, oxidizes sulphurous acid into sulphuric acid, liberates chlorine from hydrogen chloride, etc.

Upon entering into oxidation-reduction reactions, KMnO_4 (the MnO_4^- ion) can be reduced to different degrees. Depending on the pH of the solution, the product of reduction may be the Mn^{2+} ion (in an acid solution), MnO_2 (in a neutral or weakly alkaline solution) or the MnO_4^{2-} ion (in a strongly alkaline solution).

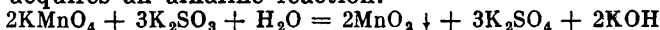
We shall illustrate these three cases by reactions between KMnO_4 and soluble sulphites. If potassium sulphite is added to a violet solution of KMnO_4 acidified with sulphuric acid, the liquid becomes almost colourless because the manganese(II) salt formed is coloured pale pink. The reaction equation is:



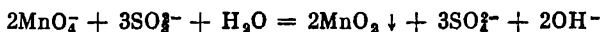
or in the net ionic form:



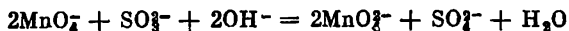
When potassium sulphite reacts with a neutral solution of potassium permanganate, the solution also loses its colour, but, in addition, a brown precipitate of manganese dioxide appears, and the solution acquires an alkaline reaction:



or in the net ionic form:

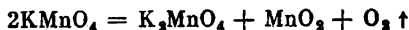


With a great alkali concentration and a small amount of the reducing agent, manganate ions form according to the equation:



Being a vigorous oxidizing agent, potassium permanganate is widely used in chemical laboratories and production processes; it is also an excellent disinfectant.

When dry potassium permanganate is heated, it decomposes already at a temperature of about 200 °C as follows:



This reaction is sometimes used in the laboratory to produce oxygen.

Free permanganic acid HMnO_4 corresponding to the permanganates has never been obtained in the anhydrous state and is known only in solution. The concentration of its solution can be brought up to 20%. It is a very strong acid that completely ionizes in an aqueous solution: its apparent degree of ionization in a 0.1 *N* solution is 93%.

Manganese(VII) oxide or *permanganic anhydride* Mn_2O_7 can be prepared by reacting concentrated sulphuric acid with potassium permanganate:



Manganese(VII) oxide is a greenish brown oily liquid. It is very unstable: when heated or upon contact with combustible substances it decomposes with an explosion into manganese dioxide and oxygen.

118. Rhenium

Rhenium does not form any independent minerals. It is contained in negligible amounts in molybdenum ores and in some rare minerals. The total content of rhenium in the Earth's crust is $1 \times 10^{-7}\%$ (mass).

Rhenium was discovered only in 1925, but its existence was predicted back in 1871 by Mendeleev, who called it *divmanganese*.

Rhenium in the free state is a pale gray metal. Its density is 21.0 g/cm³, and its melting point is about 3190 °C. It does not dissolve in hydrochloric and hydrofluoric acids, while nitric and hot concentrated sulphuric acids do dissolve it with the formation of perrhenic acid HReO_4 .

Rhenium and its alloys with tungsten and molybdenum are used in the production of electric lamps and electrical vacuum devices; they have a long service life and are stronger than tungsten. Alloys of tungsten with rhenium go to make thermocouples that can be used within a temperature range from 0 to 2500 °C. Heat-resistant

and refractory alloys of rhenium with tungsten, molybdenum, and tantalum are used to make some vital components. Rhenium and its compounds are catalysts in the oxidation of ammonia, the oxidation of methane, and the hydrogenation of ethylene.

Rhenium forms several oxides of which the most stable and typical of rhenium is rhenium(VII) oxide or perrhenic anhydride Re_2O_7 (yellowish brown plates). Its reaction with water yields a colourless solution of perrhenic acid HReO_4 whose salts are known as perrhenates. Unlike permanganic acid and its salts, oxidizing properties are not characteristic of perrhenic acid and perrhenates.

12

EIGHTH GROUP OF THE PERIODIC TABLE

NOBLE GASES

119. General

The main subgroup of Group VIII is formed by the noble gases—helium, neon, argon, krypton, xenon, and radon. These elements are characterized by their very low chemical activity, which is why they were named *noble*, or *inert gases*. They form compounds with other elements or substances with difficulty; no chemical compounds of helium, neon, and argon have been obtained. The atoms of the noble gases do not combine into molecules; in other words, their molecules are monatomic.

Each period in the periodic table terminates in a noble gas. Apart from helium, they all have eight electrons in their outer electron layer forming a very stable system. The electron shell of helium consisting of two electrons is also stable. Consequently, the atoms of the noble gases are characterized by high values of their ionization energy and, as a rule, by negative values of their energy of affinity to an electron.

Table 16 gives selected properties of the noble gases, and also their content in the air. Inspection of the table shows that the liquefaction and freezing points of the noble gases drop with their decreasing atomic masses or atomic numbers: helium has the lowest liquefaction point, and radon, the highest.

Up to the end of the 19th century, the air was assumed to consist only of oxygen and nitrogen. But in 1894, the British physicist Lord Rayleigh found that the density of nitrogen obtained from the air (1.2572 g/l) is somewhat greater than that of nitrogen prepared from its compounds (1.2505 g/l). William Ramsay, a professor of chemistry, assumed that the difference in densities is due to the presence of a heavier gas in the atmospheric nitrogen. By binding the nitrogen with red-hot magnesium (Ramsay), or making it combine with oxygen by means of an electric discharge (Rayleigh), both scientists separated a small amount of a chemically inert gas from atmospheric nitrogen. This is how the element named argon, unknown before that time, was discovered. After argon, helium, neon, krypton, and xenon, contained in the air in negligible amounts, were

Table 16

Selected Properties of the Noble Gases and Their Content in the Air

	He	Ne	Ar	Kr	Xe	Rn
Atomic radius, nm	0.122	0.160	0.192	0.198	0.218	...
Ionization energy $E \rightarrow E^+$, eV	24.59	21.56	15.76	14.00	12.13	10.75
Density in standard conditions, g/l	0.18	0.90	1.78	3.71	5.85	9.73
Liquefaction point at standard atmospheric pressure, °C	-268.9	-246.0	-185.9	-153.2	-108.1	-61.9
Freezing point, °C	-271.4*	-248.6	-189.3	-157.4	-111.85	-71
Content in air, % (volume)	0.0005	0.0016	0.93	About 10^{-4}	About 10^{-5}	About 10^{-12}

* At pressure of 3.0 MPa.

separated from it. The last element of the subgroup—radon—was discovered when studying radioactive transformations.

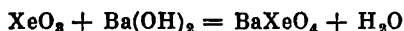
The existence of the noble gases was predicted back in 1883, i.e. 11 years before the discovery of argon, by the Russian scientist Nikolai Morozov (1854-1946), who for his participation in the revolutionary movement was in 1882 confined by the tsarist government in the Shlisselburg fortress. Morozov determined correctly the place of the noble gases in the periodic table, advanced notions on the intricate structure of an atom, and on the possibility of the synthesis of elements and the use of intratomic energy. Morozov was released from confinement in 1905, and his remarkable foresight became known only in 1907 after publication of his book "Periodic Systems of the Structure of Matter", which he had written in solitary confinement.

In 1926, Morozov was elected an honorary member of the USSR Academy of Sciences.

For a long time the atoms of the noble gases were considered incapable of forming chemical bonds with atoms of other elements. Only comparatively unstable molecular compounds of the noble gases were known such as the hydrates $\text{Ar} \cdot 6\text{H}_2\text{O}$, $\text{Kr} \cdot 6\text{H}_2\text{O}$, and $\text{Xe} \cdot 6\text{H}_2\text{O}$ formed when compressed noble gases react with freezing supercooled water. These hydrates belong to inclusion or clathrate compounds (see Vol. 1, Sec. 72); no valence bonds appear in the formation of such compounds. The formation of clathrate compounds

with water is facilitated by the presence of numerous voids in the crystalline structure of ice (see Vol. 1, Sec. 70).

In the last decades, however, it was found that krypton, xenon, and radon can combine with other elements, first of all with fluorine. For instance, the direct reaction of the noble gases with fluorine (with heating or in an electrical discharge) yields the fluorides KrF_2 , XeF_2 , KrF_4 , XeF_4 , and RnF_4 . All of them are crystals which are stable in ordinary conditions. Xenon derivatives in the oxidation state +6 have also been obtained—the hexafluoride XeF_6 , trioxide XeO_3 , and the hydroxide $\text{Xe}(\text{OH})_6$. The latter two compounds exhibit acid properties; for example, reacting with alkalis, they form salts of xenonic acid, exemplified by the reaction



Xenon(VI) derivatives are strong oxidizing agents. When they are reacted with still stronger oxidizing agents, however, compounds can be obtained in which xenon has the oxidation state +8. Known compounds of this kind include the octafluoride XeF_8 , the tetroxide XeO_4 , and the oxohexafluoride XeOF_6 .

The higher chemical activity of krypton, xenon, and radon in comparison with the first members of the group of noble gases is explained by the relatively low ionization potentials of their atoms (see Table 16). For krypton, xenon, and radon, these values are close to the ionization potentials of some other elements (for example, the ionization potential of the nitrogen atom is 14.53 V, and of the chlorine atom 12.97 V).

Argon, neon, and helium have found the greatest practical application.

120. Helium

The history of the discovery of helium is a brilliant example of the might of science. It was discovered in 1868 by two astronomers—Pierre Janssen (France) and Joseph Lockyer (Great Britain)—in studying the spectra of the Sun. A bright yellow line was detected in these spectra that was never encountered in the spectra of the elements known at that time. This line was ascribed to a new element existing on the Sun that was not known on the Earth. It was named helium from the Greek "helios"—the Sun. Almost thirty years later, Ramsay in heating the mineral cleveite obtained a gas whose spectrum was identical to that of helium. Hence, helium was discovered on the Sun before it was found on the Earth.

After hydrogen, helium is the lightest of all gases. Its mass is less than one-seventh that of air.

For a long time, helium remained the only gas that did not lend itself to liquefaction. Finally, in 1908, it was transformed into a liquid boiling at -268.9°C . Upon the evaporation of liquid helium,

a temperature was obtained only a few tenths of a kelvin higher than absolute zero. In 1926, helium was solidified for the first time. Solid helium is a transparent substance melting at -271.4°C under a pressure of 3.0 MPa.

Helium is encountered on the Earth not only in the atmosphere. Considerable amounts of it evolve at some places from the depths of the Earth together with natural gases. The waters of many mineral springs also emit helium.

Although the content of helium in the air is not great, in the Universe it occupies the second place in its abundance (after hydrogen). Spectral analysis shows the presence of this element in all stars. Its accumulation in the Universe is a result of the thermonuclear reaction of transformation of hydrogen into helium (see Sec. 1).

Helium is produced from certain natural gases in which it is contained as the product of decay of radioactive elements. It is used to create an inert medium in the gas welding of metals, and also in atomic engineering, where its chemical inertness and low ability of capturing neutrons are taken advantage of. Helium is widely used in physical laboratories as a coolant and in work in low-temperature physics. It is also employed as a thermometric substance in thermometers used in the temperature range from 1 to 80 K. The helium isotope ^3He is the only substance suitable for measuring temperatures below 1 K.

121. Neon. Argon

These gases, and also krypton and xenon, are obtained from air by separating it upon deep cooling. Argon, because of its comparatively high content in the air, is obtained in considerable amounts, the other gases—in smaller amounts. Neon and argon have found numerous applications. Both of them are used to fill incandescent lamps and gas discharge lamps; neon lamps have a red glow, and argon ones—a light blue glow. Argon, being the most available of the noble gases, is also used in metallurgical and chemical processes requiring an inert medium, particularly in the argon-arc welding of aluminium and aluminium-magnesium alloys.

SECONDARY SUBGROUP

The secondary subgroup of Group VIII includes three triads of *d* elements. The first of them is formed by the elements iron, cobalt, and nickel, the second by ruthenium, rhodium, and palladium, and the third by osmium, iridium, and platinum.

Most of the elements of this subgroup have two electrons in the outer electron layer of the atom, they are all metals. In addition to the outer electrons, electrons from the preceding incompletely

filled layer participate in the formation of chemical bonds. These elements have oxidation states of 2, 3, and 4. Higher oxidation states are rarely exhibited.

A comparison of the physical and chemical properties of the Group VIII elements shows that iron, cobalt, and nickel which are in the first large period, are very similar to one another, and at the same time greatly differ from the elements of the other two triads. This is why they are usually treated separately as the iron family. The remaining six elements of Group VIII are combined under the general name of the platinum metals.

IRON FAMILY

Table 17 gives selected properties of the iron family elements.

Table 17

Selected Properties of Iron, Cobalt, and Nickel

	Fe	Co	Ni
Atomic radius, nm	0.126	0.125	0.124
Ionization energy			
$E \rightarrow E^+$, eV	7.89	7.87	7.63
$E^+ \rightarrow E^{2+}$, eV	16.2	17.1	18.15
$E^{2+} \rightarrow E^{3+}$, eV	30.6	33.5	35.16
Radius of ion E^{2+} , nm	0.080	0.078	0.074
Radius of ion E^{3+} , nm	0.067	0.064	...
Standard enthalpy of atomization of metal at 25 °C, kJ per mole of atoms	417.0	428.4	428.8
Density, g/cm ³	7.87	8.84	8.91
Melting point, °C	1539	1492	1455
Boiling point, °C	2870	3100	2900
Standard electrode potential of process $E^{2+} + 2e^- = E$, V	-0.440	-0.277	-0.250

122. Iron (*Ferrum*). Occurrence

Iron is the most abundant metal on the globe after aluminium, forming 4 % (mass) of the Earth's crust. It is found in the form of a variety of compounds: oxides, sulphides, and silicates. It occurs in the free state only in meteorites.

The most important iron ores include magnetite Fe_3O_4 , red iron ore or hematite Fe_2O_3 , brown iron ore or limonite $2Fe_2O_3 \cdot 3H_2O$, and spathic iron ore or siderite $FeCO_3$. Iron pyrites, or simply pyrite FeS_2 , encountered in large amounts is rarely used in metallurgy because iron of a very low quality due to the high sulphur content is produced from it. But pyrite nevertheless has an important appli-

cation—it is the starting material in the production of sulphuric acid (see Sec. 17).

In the USSR, deposits of iron ores are found in the Urals, where whole mountains (for example Magnitnaya, Kachkanar, and Vyso-kaya) are formed of magnetite of an excellent quality. Deposits just as rich are in the Krivoi Rog Region and on the Kerch Peninsula, the former being red iron ore, and the latter brown ore. Great deposits of iron ores have been found near Kursk, on the Kola Peninsula, in Western and Eastern Siberia, and in the Far East. The total amount of iron ores in the USSR is more than half of all the world's reserves.

123. Iron and Its Alloys in Engineering. The Development of Metallurgy in the USSR

Iron is the most important of all the metals produced. All modern engineering is associated with the use of iron and its alloys. The tremendously important role played by iron can be seen from the fact that the amount of iron extracted is about 15 times greater than that of all the other metals taken together.

Up to the 19th century, the known iron alloys were only those with carbon—various irons and steels. Later, however, new iron-based alloys were developed containing chromium, nickel, and other elements. At present, iron alloys are divided into carbon steels, irons, alloyed steels, and steels with special properties (see Sec. 127).

In engineering, iron alloys (including steels) are customarily known as ferrous metals, and their production as ferrous metallurgy.

The production of iron grew especially rapidly in the last century. At the beginning of the 19th century, the world's production of iron was only 0.8 million tonnes a year, while at the end of the century it was already 66 million tonnes a year. In 1962, the capitalist countries produced 176 million tonnes of iron and ferroalloys, and 245 million tonnes of steel.

Tsarist Russia lagged greatly behind the industrially developed countries in the production of ferrous metals. The Russian iron and steel industry produced only 4.2 million tonnes of iron and the same amount of steel in 1913. After the first world war, the production of iron dropped sharply, and in 1920 it was only 2.7% of the 1913 figure. The restoration of the iron and steel industry conducted in exclusively difficult conditions required enormous efforts and a long time: only in 1929 did the production of steel reach the 1913 level.

Rapid development of Soviet metallurgy began during the years of the first five-year plans. The metallurgical industry in the south of the European part of the USSR was completely reconstructed, and a new coal and metallurgical base was set up in the eastern regions of the country. Major iron and steel works such as the Magni-

togorsk and Kuznetsk ones were erected. Already by the end of the first five-year period, the production of iron reached 147% in comparison with the 1913 level. After reaching the prerevolutionary level of iron production in 1929, Soviet iron and steel workers increased the production of iron almost 3.5 times during the next eight years. For such a growth, the iron and steel industry of the USA had required 20 years, and of Germany—23 years.

The growth of Soviet metallurgy in recent years is characterized by the following data:

Year	1949	1959	1969	1977
Production, million tonnes:				
iron	16.4	43.0	81.6	107
steel	23.3	60.0	110	147

Such rates of growth were due both to the erection of new works and to the intensification of production as a result of the constantly growing use of natural gas and oxygen in ferrous metallurgy.

The ore base of metallurgy has also grown in recent years—new iron ore deposits were developed in Kazakhstan, Siberia, and in the region of the Kursk Magnetic Anomaly. The iron ore extracted in 1977 reached 240 million tonnes.

124. Physical Properties of Iron.

Phase Diagram of Iron-Carbon System

In the thirties of the 19th century, the Russian engineer P. Anosov for the first time used a microscope to study the structure of steel and its changes after forging and heat treatment. In the sixties of the 19th century, similar investigations were undertaken in other countries.

In 1868, D. Chernov first pointed out the existence of definite temperatures ("critical points") depending on the carbon content of steel and characterizing the transformations of one microstructure of steel into another. This laid the cornerstone of studying the Fe-C phase diagram, while 1868 became the year in which physical metallurgy—the science dealing with the structure and properties of metals and alloys, was born. The French investigator F. Osmond used the pyrometer that had just been invented by Le Chatelier to determine the values of the critical points more accurately. He described the nature of the microstructural changes observed in the transition through these points, and named the most important structures of iron-carbon alloys; these names are still in use. Since that time, scientists of various countries performed an enormous amount of investigations devoted to iron-carbon alloys and to the phase diagram of the Fe-C system. Such investigations are still being conducted. Their aim is to determine more exactly the

positions of the lines in the phase diagram in connection with the use of purer substances and more accurate and up-to-date methods.

The melting point of iron is $1539 \pm 5^\circ\text{C}$. Iron forms two crystal-line modifications: α -iron and γ -iron. The former has a cubic body-centred lattice, the latter—a cubic face-centred lattice. Alpha-iron is thermodynamically stable within two temperature intervals: below 912°C and from 1394°C to the melting point. Between 912 and 1394°C , γ -iron is stable. The temperature intervals of the stability of α - and γ -iron are due to the nature of the change in the Gibbs energy of the two modifications when the temperature changes (see Fig. 62). At temperatures below 912 and above 1394°C , the Gibbs energy of α -iron is less than that of γ -iron, while in the interval from 912 to 1394°C it is greater.

The temperatures of the phase transitions of iron can be seen quite clearly on the cooling curve in the form of steps—horizontal portions (see Fig. 63). A glance at the figure shows that in addition to the steps corresponding to the points listed above, the cooling curve has another step—at 768°C . This temperature is associated not with transformation of the lattice, but with a change in the magnetic properties of α -iron. Above 768°C , iron is not magnetic, while below this temperature it is magnetic. Non-magnetic α -iron is sometimes called β -iron, and the modification of α -iron that is stable at a temperature from 1392°C to the melting point— δ -iron.

Iron is a silvery plastic metal. It lends itself well to forging, rolling, and other kinds of mechanical processing. The mechanical

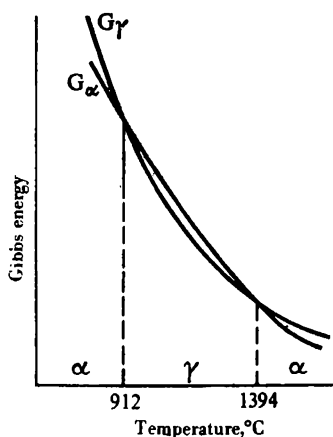


Fig. 62. Temperature dependence of Gibbs energy of α -iron (G_α) and γ -iron (G_γ)

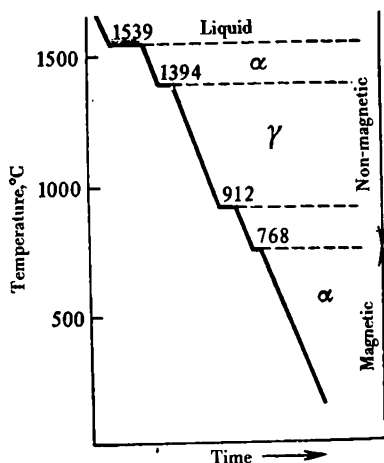


Fig. 63. Cooling curve of iron

properties of iron depend greatly on its purity—on the presence of even small amounts of other elements in it.

Solid iron is capable of dissolving many elements. Particularly, carbon dissolves in iron. Its solubility depends greatly on the crystalline modification of iron and on the temperature. Carbon dissolves very insignificantly in α -iron, and much better in γ -iron. The carbon solution in γ -iron is thermodynamically stable within a broader temperature interval than pure γ -iron. A solid solution of carbon in α -iron is called ferrite, and in γ -iron, austenite.

The chemical compound iron carbide, or cementite Fe_3C corresponds to a carbon content of 6.67% (mass) in iron. This substance has a complex crystalline structure and is characterized by a high hardness (close to that of diamond) and brittleness. Cementite melts at a temperature of about 1600°C^* .

The mechanical properties of ferrite and austenite depend on their carbon content. At all carbon concentrations, however, ferrite and austenite are not as hard as cementite and are more plastic than it.

A phase diagram of the iron-carbon system giving a notion of the structure of iron-carbon alloys is very important. It helps to explain how the properties of steels and irons depend on their carbon con-

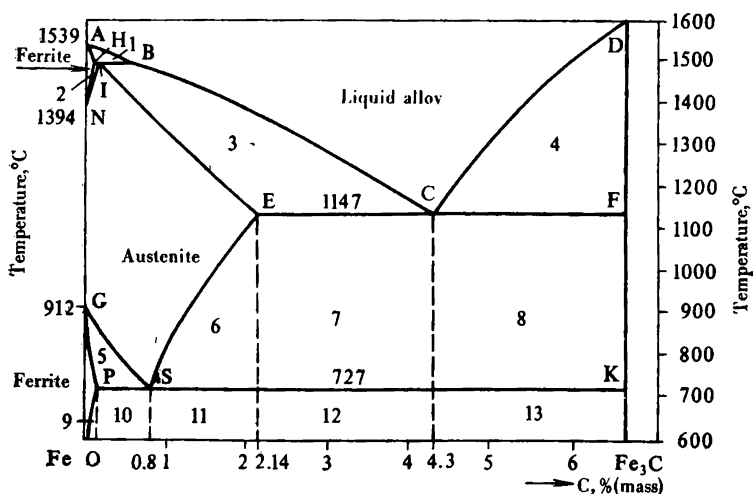


Fig. 64. Phase diagram of iron-carbon system

* Cementite is not thermodynamically stable in all the conditions corresponding to the phase diagram of the system Fe-C. But the decomposition of cementite attended by the separation of graphite proceeds so slowly in the majority of cases that it practically does not occur. Graphite separates only when iron is formed in definite conditions (see p. 362).

tent and heat treatment. It is the basis for choosing iron-carbon alloys having definite preset properties. Figure 64 gives a part of the phase diagram of the system Fe-C corresponding to a carbon concentration from 0 to 6.67% or, which is the same, from pure iron to the carbide Fe_3C . This is the most important part of the diagram because iron alloys containing not over 5% of carbon have a practical significance.

The phase diagram of the system Fe-C is more complicated than the main kinds of phase diagrams for metal systems dealt with in Chapter 6. But all its points, curves, and regions are similar to those described in Sec. 81. Its features are due to the circumstances mentioned above: the existence of two modifications of crystalline iron, the ability of both these modifications to form solid solutions with carbon, and the ability of iron to enter into a chemical compound with carbon to form cementite.

The left-hand vertical axis of the diagram corresponds to pure iron, the right-hand one to the carbide Fe_3C (cementite). Points *A* and *D* show the melting points of iron and the carbide, points *G* and *N*—the temperatures of transition of α -iron into γ -iron and vice versa.

Line *ABCD* is a curve showing the temperatures of the beginning of crystallization of the liquid alloys, and line *AHIECF* is a curve showing the temperatures of the beginning of melting of the solid alloys. All lines below the latter curve correspond to equilibria between the solid phases.

The region above line *ABCD* corresponds to a liquid alloy. The regions adjoining the left-hand vertical axis correspond to solid solutions of carbon in iron: line *AHN* confines the region of a solid solution of carbon in α -iron at high temperatures (the region of high-temperature ferrite), line *NIESG* confines the region of a solid solution of carbon in γ -iron (the austenite region), line *GPO* confines the region of a solid solution of carbon in α -iron at low temperatures (the region of low-temperature ferrite). Homogeneous systems correspond to these regions: the structure of both the liquid and the solid solutions is homogeneous in each of these phases.

Heterogeneous systems—mixtures of crystals of two phases or of crystals and a liquid—correspond to the remaining regions in the diagram.

Let us consider the most important transformations occurring upon the slow cooling of liquids of various concentrations. This will help us see what alloys correspond to the regions of heterogeneity of the diagram.

Assume that we have a liquid containing 0.8% of carbon. Its crystallization begins at point 1 (Fig. 65). When the liquid is cooled to a temperature corresponding to this point, crystals of austenite will separate; their composition corresponds to point 2. The melt

becomes rich in carbon, and its composition changes along line BC . The composition of the crystals in the course of crystallization changes along curve IE . When the composition of the crystals reaches point 3 , crystallization terminates. As always in the formation of a solid solution, a diffusion process occurs simultaneously in the solid phase, as a result of which upon slow cooling the composition of all the crystals is the same.

Further, the austenite formed cools without any transformations to point S (see Fig. 64). This point (a temperature of 727°C) shows the minimum temperature of the stable existence of austenite. At 727°C , its eutectoid decomposition occurs*. The forming eutectoid consists of alternating small plates of ferrite and cementite. When a fracture of it is observed under a microscope, it reminds one of mother-of-pearl. This is why such a structure—a eutectoid mixture of ferrite and cementite—has been called **pearlite**.

If the initial liquid contains not 0.8% carbon, but somewhat less, for example 0.7% , the austenite formed upon crystallization begins to decompose not at 727°C , but at a higher temperature (point 1 in Fig. 66). The transformation begins with the separation of ferrite crystals (point 2 in Fig. 66) whose carbon content is very low. Consequently, the remaining austenite becomes richer in carbon, and upon further cooling its composition changes along curve GS . When point S is reached, eutectoid transformation at constant temperature begins, and upon its completion the steel will consist of ferrite and

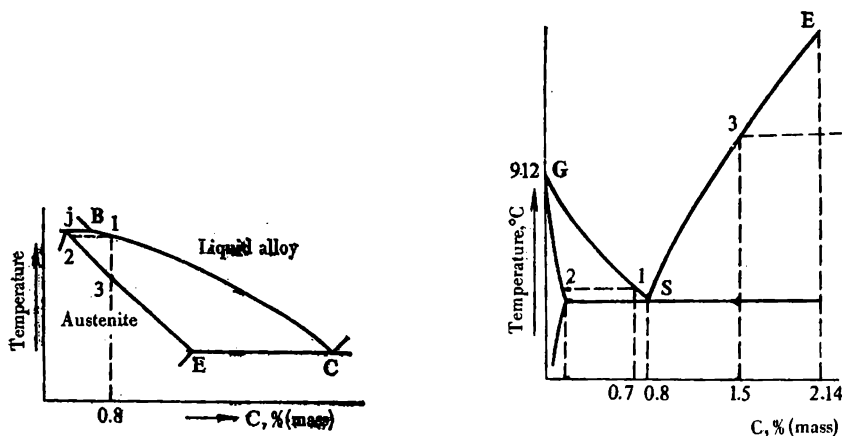


Fig. 65. Part of phase diagram of Fig. 66. Part of phase diagram of iron-carbon system

* Eutectoid decomposition leading to the formation of a eutectoid is a process similar to the crystallization of a eutectic. The difference is that a eutectic is formed from a liquid alloy, i.e. a liquid solution, whereas a eutectoid is formed from a solid solution.

pearlite. It follows from the above that a mixture of a liquid alloy with austenite crystals corresponds to region 3 in the diagram (see Fig. 64), a mixture of ferrite and austenite crystals corresponds to region 5, and a mixture of pearlite with ferrite crystals to region 10.

If the initial liquid contains over 0.8% carbon (but less than 2.14%), for instance 1.5%, the decomposition of the austenite begins with the separation of cementite (point 3 in Fig. 66). Owing to the separation of Fe_3C —a phase rich in carbon—the remaining austenite becomes rich in iron so that upon further cooling its composition changes along curve ES . At point S , the separation of pearlite begins. The result is steel with a structure consisting of cementite and pearlite. Hence, a mixture of cementite and austenite crystals corresponds to region 6 in the diagram (Fig. 64), and a mixture of pearlite with cementite crystals corresponds to region 11.

Let us now turn to alloys containing over 2.14% carbon. Primary crystallization in this case terminates in a eutectic transformation at 1147 °C when a eutectic mixture of austenite and cementite separates from the liquid containing 4.3% carbon (point C in Fig. 64). If we proceed from a liquid having the eutectic composition (4.3% C), crystallization begins and terminates at the same temperature of 1147 °C. For alloys containing less than 4.3% carbon (but greater than 2.14%), the separation of austenite will precede the formation of the eutectic. With a carbon content above 4.3%, crystallization begins with the separation of cementite, but when point C is reached in the diagram, the formation of the eutectic is also observed. Consequently, as a result of the crystallization of liquid alloys containing over 2.14% carbon, a structure is initially obtained consisting either only of the eutectic, or of the eutectic with crystals of austenite or cementite.

At the same time, as we have seen earlier, in the crystallization of liquid alloys containing less than 2.14% carbon, austenite is initially obtained. This difference in structure at high temperatures creates the difference in the technological and mechanical properties of alloys. The eutectic makes alloys lose their malleability, but its low melting point facilitates the use of high-carbon alloys as foundry materials. *Iron and carbon alloys containing less than 2.14% carbon are called steels, and those containing more than 2.14% carbon—irons, or commercial irons.*

This boundary (2.14% carbon) relates to iron and carbon alloys containing no other elements. In the presence of a third element, the form of the phase diagram changes, in particular the boundaries of stability of austenite in some cases shift towards low temperatures.

Let us complete our treatment of the transformations occurring in irons when they cool to below 1147 °C. At this temperature, the solubility of carbon in γ -iron is the greatest. Consequently, by the

moment of completion of the primary crystallization, the austenite contained in the iron is the richest in carbon (2.14%). Upon cooling below this temperature, the solubility of carbon in the austenite drops (curve *ES* in Fig. 64), and carbon separates from it, usually transforming into cementite. When a temperature of 727 °C is reached, all the remaining austenite, including that in the eutectic, transforms into pearlite. It follows from what has been said that a mixture of the eutectic with austenite and cementite crystals formed in the decomposition of the austenite corresponds to region 7, and a mixture of the eutectic with cementite crystals corresponds to region 8. Since at temperatures below 727 °C, the austenite of the eutectic transforms into pearlite, a mixture of pearlite and cementite corresponds to regions 12 and 13, the same as to region 11. But the alloys belonging to these two regions differ somewhat in their structure. The difference is explained by the fact that the cementite of the alloys of region 13 is formed in initial crystallization, and of region 12 in the decomposition of the austenite. Thus, at temperatures below 727 °C, iron consists of cementite and pearlite. As we shall see in Sec. 127, iron can also have a different structure.

In considering the transformations occurring in the cooling of liquid alloys of various compositions, we were able to reveal what alloys correspond to different regions of the diagram. But we have not considered all the regions of the diagram. Using the same method, it is not difficult to show which alloys correspond to the other regions: a mixture of the liquid alloy and crystals of high-temperature ferrite corresponds to region 1, a mixture of crystals of high-temperature ferrite and austenite corresponds to region 2, a mixture of a liquid alloy and cementite crystals to region 4, and a mixture of ferrite and cementite crystals to region 9.

125. Production of Iron and Steel

Iron found industrial application even before our era. In ancient times, it was produced in the soft plastic state in crucibles or furnaces using charcoal as the fuel. The slag was separated by forcing it out of the spongy iron with blows of a hammer.

With the development of iron production techniques, the temperature of the process was gradually increased. The metal and the slag began to melt; it became possible to separate them much more completely. But simultaneously, the content of carbon and other admixtures in the metal increased—the metal became brittle and unmalleanable. This is how commercial iron was produced.

Later, people learned how to convert iron; a two-stage process of producing iron from its ores appeared. In principle, it has been retained up to our time: the modern scheme of steel production consists of a blast-furnace process, in the course of which what is known

as **blast-furnace iron** or **pig iron** is produced from ore, and of a steel-melting conversion that lowers the amount of carbon and other impurities in the metal.

The modern high level of the metallurgical production process is based on theoretical investigations and discoveries made in different countries, and on rich practical experience. Quite a significant role in this progress belongs to Russian and Soviet scientists. For instance, P. Anosov founded the theory of the production of cast steel. Academicians A. Baikov, M. Pavlov, and I. Bardin are the authors of very important theoretical works on blast-furnace and steel production processes.

New technological processes for producing iron and steel have been developed during recent years in the USSR. Soviet iron and steel workers were the first to widely introduce natural gas for blast-furnace operation. Modern blast furnaces with a volume of 1300 m³ were placed into service in the USSR earlier than in the USA, while at present furnaces with a volume of 5000 m³ are in operation.

During a short historical time interval, the USSR has advanced to the second place in the world in the production of ferrous metals.

Pig iron is produced in enormous blast furnaces laid using refractory brick and reaching 30 metres in height with an internal diameter of about 12 metres.

A cross section of a blast furnace is shown schematically in Fig. 67. Its upper half is called a **shaft** and terminates at the top in an opening—the **throat**, which is closed with the aid of a movable hopper—the **top seal**. The widest part of the furnace is called the **bosh**, and its bottom part—the **hearth** or **crucible**. A blast of hot air or oxygen is blown into the furnace through special openings in the hearth (**tuyeres**).

A blast furnace is first charged with coke, and then with alternating layers of agglomerate and coke. Agglomerate is a sinter of ore and flux (see below) prepared in a definite way. Combustion and the temperature required for melting the iron are maintained by blowing heated air or oxygen into the hearth. The blast is fed into an annular pipe surrounding the bottom part of the furnace, and thence through bent pipes and the tu-

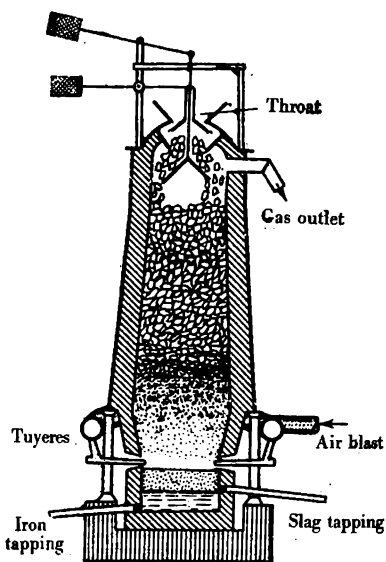
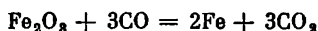


Fig. 67. Blast furnace cross section

yers into the hearth. In the latter, the coke burns to form CO_2 , which rises and passes through the layers of heated coke, reacting with the latter to form CO . This carbon monoxide reduces the major part of the ore, transforming again into CO_2 .

The ore reduction process occurs chiefly in the upper part of the shaft. It can be expressed by the net equation:



The individual steps of the process are shown in the form of reaction equations in Fig. 68.

The barren rock in the ore is mainly formed by silicon dioxide SiO_2 , which is a refractory substance. A flux is added to the ore to transform the refractory admixtures into more fusible compounds. Generally, CaCO_3 is used as the flux. When it reacts with the SiO_2 , the product formed is CaSiO_3 that readily separates as a slag.

In the reduction of the ore, the iron is obtained in the solid state. It gradually sinks into the hotter part of the furnace—the bosh—and dissolves carbon; pig iron is formed. The latter melts and flows into the bottom part of the hearth, while the molten slags gather on the surface of the iron, preventing its oxidation. The iron and slags are tapped, as they accumulate, through special holes or notches, plugged with clay when not needed.

The gases leaving the furnace outlet contain up to 25% of CO . They are burned in special apparatuses known as Cowper stoves intended for preliminarily heating the air blown into the furnace.

A blast furnace operates continuously. As the top layers of ore and coke sink, new portions are added to the furnace. A mixture of ore and coke is delivered by skip cars to the top platform of the furnace and is charged into a cast iron bell and hopper closed at the bottom by the top seal. When the latter is lowered, the mixture drops into the furnace. The operation of a furnace continues several years until it requires general overhauling.

The production of iron can be accelerated by using oxygen in

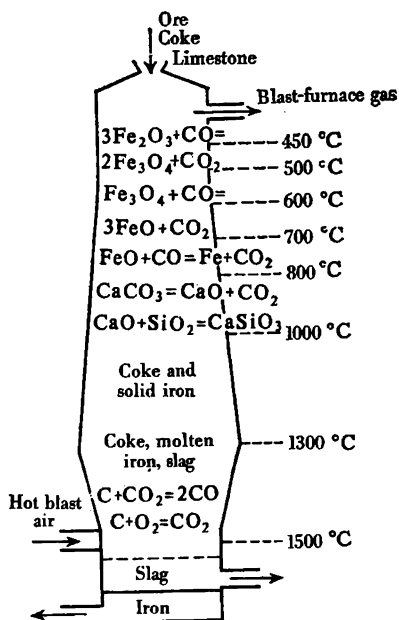


Fig. 68. Diagram of chemical reactions proceeding at different levels of a blast furnace

blast furnaces. When air enriched with oxygen is blown into a blast furnace, its preliminary heating is superfluous, owing to which there is no need to erect the intricate and cumbersome Cowper stoves, and the entire metallurgical process is considerably simplified. This is attended by a sharp growth in furnace output and a decrease in fuel consumption. A blast furnace using an oxygen blast produces 1.5 times more metal and uses only three-fourths of the coke needed with an air blast.

A modern blast furnace is a powerful and highly productive aggregate. It processes enormous amounts of materials. A furnace with a volume of 2000 m³ uses about 7000 tonnes of agglomerate and 2000 tonnes of coke a day. The product is 4000 tonnes of iron. In other words, a large blast furnace produces about 2.5 tonnes of pig iron a minute.

There are several ways of converting pig iron into steel. They are based on oxidizing the carbon and impurities contained in the iron and separating the oxides into the gaseous phase or the slag. In the USSR, the main part of the pig iron is converted into steel by the open hearth process.

The **open hearth process**, invented by the French engineer Pierre Martin, is conducted in a flame-contact reverberating furnace. The latter is charged with pig iron, and also with steel scrap requiring remelting, and some ore. Preheated air and fuel (in the form of a gas or sprayed liquid) are fed into the furnace. Combustion of the fuel produces a flame with a temperature of 1800 to 1900 °C. The metal and ore melt, and additions needed to obtain steel of the required composition are introduced into the melt. The impurities burn out mainly at the expense of the oxygen of the air.

A small amount of steel is melted in converters. The essence of the converter or, after the name of its inventor, the **Bessemer process** consists in blowing a stream of air through molten pig iron. The carbon and impurities burn out and are removed in the form of gases or pass into the slag. A converter is a pear-shaped vessel turning on a horizontal axis. The molten iron is poured in and the steel obtained is poured out in the horizontal position of the converter, while air is blown through it in its vertical position.

The converter process has a number of shortcomings in comparison with the open hearth one. The quality of Bessemer steel is lower than that of open hearth steel because an appreciable amount of nitrogen dissolves in the metal in the course of blowing air through it. This underlies the inclination of Bessemer steel to age—lose its plasticity with time and gain brittleness. Bessemer steel of a much higher quality is produced when an oxygen blast is used.

The most refined industrial process for producing steel is by **melting in electrical furnaces**. Most grades of special steels are produced by this process at present. It is easy to provide a rapid eleva-

tion of the temperature and its accurate control in an electrical furnace; an oxidizing, reducing, or neutral atmosphere can be created in it. This allows metallurgists to produce steel with the lowest content of harmful impurities; at the same time, the preset composition of the steel is ensured with a high accuracy.

In all the processes used to produce steel, the molten metal contains a small amount of dissolved oxygen (up to 0.1%). When the steel crystallizes, the oxygen reacts with the dissolved carbon to form carbon monoxide. This gas (and also some other gases dissolved in molten steel) separates from the steel in the form of bubbles. In addition, oxides of iron and the impurity metals separate along the boundaries of the grains. All this detracts from the mechanical properties of the steel.

This is why a steel melting process usually terminates in its deoxidation—diminishing of the amount of oxygen dissolved in the molten steel. There are various ways of deoxidizing steel. The one in greatest favour is the addition to the steel of small amounts of elements actively combining with oxygen. The deoxidizing agents generally used are manganese, silicon, aluminium, and titanium. The oxides of these elements formed pass into the slag.

Well deoxidized steel solidifies quietly, without the evolution of gases, and is called killed. When undeoxidized or incompletely deoxidized steel cools, gases evolve from it, and the metal seems to boil; such steel is called rimming or open. Killed steel is better than rimming steel. But rimming steels are cheaper and also find a variety of applications.

Melted steel is tapped into a pouring or teeming ladle and is poured into metal moulds, or is delivered for continuous casting. The steel solidifies in the form of ingots whose shape depends on what they are to be used for.

When steel crystallizes, it diminishes in volume, and a void known as a shrinkage cavity forms in the top part of an ingot that solidifies last of all. The portion of the ingot below a shrinkage cavity has a loose structure. No shrinkage cavities are formed in rimming ingots, but they are penetrated by a large number of bubbles. Ingots also have other defects, particularly non-homogeneity of their chemical composition. It is due to the fact that the crystals formed first contain a minimum amount of impurities, while the last portions of the crystallizing steel contain the maximum amount of them; diffusion of the impurity atoms that could level out their concentrations does not have time to occur because an ingot cools rapidly.

To eliminate ingot defects, the major part of all the steel produced (about 90%) is processed under pressure. The structure of the steel becomes substantially more homogeneous, the result being an improvement in its mechanical properties.

There is a variety of processes for pressure treatment. They include rolling, drawing, and pressing. The most important kind of pressure treatment is rolling. Ingots delivered to the rolling department of an iron and steel works are heated to 1000-1300 °C. The steel transforms into the austenite state, and its plasticity grows greatly. The heated ingots are fed to the rolling mill. It is a group of machines whose main purpose is to deform the metal by means of rotating rolls. An ingot gripped by the rolls is squeezed. The thickness of the blank diminishes, while its length grows; the operation is repeated many times. Different rolling mills produce a variety of products: plates, sheets, tubes, rails, beams, and articles having a more intricate shape, such as railway vehicle wheels. Part of the steel is rolled not to a finished product, but only to a semifinished one (plates, bars, etc.). Such a semifinished product is later processed by other methods. Hot-rolled steel is the most widely used material for the production of machines, machine tools, structural members, and consumers' goods.

126. Heat Treatment of Steel

By the heat treatment of steel is meant the change in its structure, and, consequently, in its properties achieved by heating to a definite temperature, holding at this temperature, and cooling at a definite rate. The heat treatment of steel is an exceedingly important operation in the technology of steel; it can change its properties very greatly. Both finished articles, mainly tools and machine components, and semifinished ones, for instance, castings and rolled blanks, are subjected to heat treatment.

Different kinds of heat treatment are used which impart various properties to steel. The most important of them are hardening and tempering.

Hardening is performed by heating steel to a temperature somewhat higher than that of transformation of pearlite into austenite, holding it at this temperature, and rapidly cooling it. Hardening makes steel hard and strong, but at the same time makes it brittle. This is why hardened steel is usually subjected to another operation—tempering. It consists in heating the steel to a temperature at which it does not yet transform into austenite, holding it at this temperature, and comparatively slowly cooling it. Tempering is the final operation of heat treatment. As a result of hardening and tempering conducted according to preset conditions, steel acquires the essential mechanical properties.

What processes occur in steel when it is hardened and tempered? To answer this question, let us revert to the phase diagram of the Fe-C system. Figure 69 gives a part of this diagram corresponding to a carbon content up to 2.14% and a temperature up to 1147 °C.

When steel of a eutectoid composition (0.8% carbon) is heated, pearlite at 727 °C transforms into austenite. When steel containing a smaller amount of carbon, for instance 0.4%, is heated (the structure of such steel consists of pearlite and ferrite), at 727 °C the pearlite transforms into austenite with 0.8% carbon (point 1 in Fig. 69), while upon further heating, the ferrite gradually dissolves in the austenite; the carbon content in the austenite diminishes along line *SG*. When point 2 is reached, the ferrite vanishes, and the concentration of the carbon in the austenite becomes equal to its total content in the steel.

The transformations occur similarly for steel containing larger amounts of carbon, for example 1.4%. Such steel consists of pearlite and cementite. At 727 °C, the pearlite transforms into austenite containing 0.8% carbon (point 3), while upon further heating, the cementite dissolves in the austenite. When point 4 is reached, the cementite vanishes, and the carbon content in the austenite becomes equal to 1.4%.

Thus, the first stage of hardening—heating—is attended by the transformation of the steel to the state of austenite. The diffusion of atoms even at high temperatures occurs in a solid far from instantaneously. For completeness of the transformation, the steel is held for a certain time at a temperature somewhat higher than the corresponding point on line *GS* or *SE*.

The processes occurring in the slow cooling of austenite are the reverse of those we have just considered. But when the steel is cooled rapidly, these processes associated with the diffusion of the carbon and iron atoms do not have time to occur. As a result, the steel is in a non-equilibrium state.

Upon cooling, the austenite becomes a thermodynamically unstable phase; at temperatures below 727 °C, pearlite or pearlite with an excess of ferrite or cementite is thermodynamically stable. An increase in supercooling increases the difference between the Gibbs energies of the austenite and pearlite stimulating the transformation. But at the same time, greater supercooling (i.e. a lower temperature) retards the diffusion of the atoms. As a result of the simultaneous action of these opposite trends, the rate of transformation of austenite into pearlite is maximum at slight

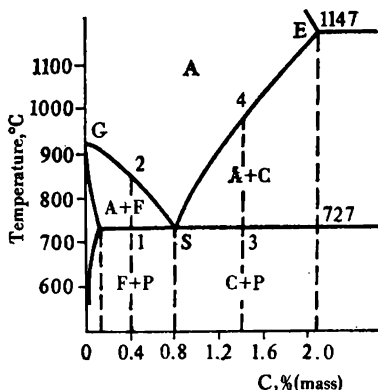


Fig. 69 Part of phase diagram of iron-carbon system
A—austenite; *F*—ferrite;
C—cementite; *P*—pearlite

supercoolings, i.e. when the temperature is lowered slowly. At great supercoolings, however, when the temperature is rapidly lowered, the rate of the diffusion processes approaches zero, and the transformation becomes impossible. The crystal lattice of iron, however, changes its structure at any rate of cooling, so that as a result of lowering of the temperature, γ -iron transforms into α -iron. Hence, the hardening of steel is based on the transformation of austenite into a supersaturated solid solution of carbon in α -iron. This phase is called **martensite**; being thermodynamically unstable, it is not reflected in the phase diagram.

If in the equilibrium state, the solubility of carbon in α -iron at 20 °C does not exceed 0.0025%, in martensite it is the same as in the initial austenite. The martensite transformation is not attended by the diffusion redistribution of the carbon, i.e. the displacements of the carbon and iron atoms do not exceed the interatomic distances in the course of this transformation. What does occur is only a rearrangement of the cubic face-centred lattice of the γ -iron into the cubic body-centred lattice of α -iron. But the retaining of carbon atoms in the new lattice leads to its distortion, and more exactly, to transformation into a tetragonal system with a ratio of the axes that only insignificantly differs from unity. When the carbon content in the steel exceeds 0.5%, a part of the austenite does not undergo transformations and is retained in the hardened steel.

Martensite has a high hardness that grows with an increase in the carbon content. Its hardness is due to the very fine non-homogeneity of the structure preventing the shifting of dislocations. But at the same time, owing to the large internal stresses appearing when it is formed, martensite is brittle. This is why hardened steel is hard, but brittle.

In tempering, martensite and the residual austenite partly decompose. The degree of transformation of the martensite and the structure of the products formed depend on the heating temperature in tempering.

In low-temperature tempering, the articles are heated to 150-250 °C. The carbon separates only partly from the martensite, forming inclusions of iron carbide plates (cementite). Low-temperature tempering diminishes the internal stresses in steel and improves its strength, while its hardness and wear-resistance remain unchanged. Cutting tools and measuring instruments are subjected to this kind of tempering.

Moderate-temperature tempering is conducted at 350 to 500 °C. At these temperatures, the diffusion of the carbon and iron atoms proceeds sufficiently rapidly; the carbon separates completely from the martensite, and the steel acquires the structure of ferrite and thin-laminar particles of cementite. It becomes elastic, which

is why helical and leaf springs are subjected to moderate-temperature tempering.

Tempering conducted at 500 to 680 °C is called **high-temperature** or **high**. At these temperatures, the crystallites of iron carbide grow—its thin plates consolidate and acquire a round shape. High tempering increases the toughness of steel; its strength and hardness diminish somewhat, but nevertheless remain quite high. In high tempering, the best relationship between the mechanical properties of steel is created. This is why hardening with high tempering is called **toughening** of steel. Toughening is the main kind of heat treatment of structural steels (see next page).

Sometimes, the surface of an article or component must have mechanical properties differing from those in its bulk. For example, a motor vehicle axle must have a hard surface well resisting wear, and at the same time it must not be brittle, i.e. it must have a certain elasticity to prevent fractures in jolts. In such cases, **chemical heat treatment** of steel is employed, i.e. the surface of an article is saturated with carbon, nitrogen, or some other elements, which is achieved by diffusion of the element from the surrounding medium at elevated temperatures. Saturation with carbon, or **case-hardening**, is conducted by heating an article in an atmosphere of CO, CH₄, or in activated carbon. The surface layer of the steel from 0.5 to 2 mm deep acquires a great hardness and strength, whereas the remaining part of the steel remains tough and elastic. In **nitriding** of steel, i.e. in saturating its surface with nitrogen, an article is subjected to prolonged heating in an ammonia atmosphere at 500 to 600 °C. Nitrided steel has a still greater hardness than case-hardened steel owing to the formation of iron nitrides in the surface layer. It withstands heating up to 500 °C without losing its hardness.

127. Iron Alloys

We have already mentioned that alloys of iron with carbon are grouped into steels and commercial irons. Steels, in turn, are grouped in accordance with their chemical composition and application, and commercial irons—according to the state of the carbon in them.

As regards their chemical composition, carbon and alloy steels are distinguished.

Carbon steels are alloys of iron with carbon, the content of the latter not exceeding 2.14%. Commercial carbon steel, however, always contains admixtures of many elements. The presence of some admixtures is due to the features of steel production: for example, in deoxidation (see p. 355), small amounts of manganese or silicon are introduced into the steel. They partly pass into the slag as oxides, and partly remain in the steel. Other admixtures pass into the pig iron in small amounts from the initial ore, and

then into the steel. It is difficult to eliminate them completely, and carbon steels, for example, usually contain from 0.05 to 0.1% phosphorus and sulphur.

The mechanical properties of slowly cooled carbon steel depend greatly on its carbon content. Slowly cooled steel consists of ferrite and cementite, the amount of the cementite being proportional to the carbon content. The hardness of cementite is much greater than that of ferrite. Consequently, with a growth in the carbon content in steel, its hardness increases. In addition, the cementite particles hinder the motion of the dislocations in the main phase—in the ferrite. For this reason, an increase in the carbon content lowers the plasticity of steel.

Carbon steel has a very broad application. Depending on its use, steel with a low or a higher carbon content is employed, without heat treatment (in the "raw" form—after rolling), or with hardening and tempering.

Alloy Steels. Elements specially introduced into steel in definite concentrations to change its properties are called **alloying elements**, and the steel containing such elements is called **alloy steel**. The most important alloying elements include chromium, nickel, manganese, silicon, vanadium, and molybdenum.

Different alloying elements change the structure and properties of steel in different ways. For instance, some elements form solid solutions in γ -iron that are stable in a broad range of temperatures. For example, solid solutions of manganese or nickel in γ -iron with a considerable content of these elements are stable from room temperature to the melting point of the alloy. Alloys of iron with such metals are therefore called **austenite steels** or **austenite alloys**.

The influence of alloying elements on the properties of steel is also due to the fact that some of them form carbides with carbon that may be simple, for instance, Mn_3C and Cr_7C_3 , or complex (double), for instance $(\text{Fe}, \text{Cr})_3\text{C}$. The presence of carbides, especially in the form of dispersed inclusions in the structure of the steel, often appreciably affects its mechanical and physicochemical properties.

According to their application, steels are divided into structural, tool, and steels with special properties. **Structural steels** are used for making machine components and structural members. Both carbon and alloy steels are used as structural ones. Structural steels have a high strength and plasticity. At the same time, they must lend themselves well to pressure treatment, cutting, and welding. The main alloying elements of structural steels are chromium (about 1%), nickel (1-4%), and manganese (1-1.5%).

Tool steels are carbon and alloy steels having a high hardness, strength, and wear resistance. They are employed for making cutting tools, measuring instruments, punches, and dies. The required hard-

ness is ensured by the carbon contained in these steels (from 0.8 to 1.3%). The main alloying element of tool steels is chromium; sometimes tungsten and vanadium are also introduced into them. A special group of tool steels is formed by high-speed steels retaining their cutting properties at high cutting speeds when the temperature of the working part of the cutting tool increases from 600 to 700 °C. The chief alloying elements of this steel are chromium and tungsten.

Steels with Special Properties. This group includes stainless, heat-resistant, high-temperature, magnetic, and some other steels. Stainless steels are stable against corrosion in the atmosphere, moisture, and in acid solutions, heat-resistant steels are stable in corrosion-active media at elevated temperatures. High-temperature steels retain their high mechanical properties when heated to considerable temperatures, which is important in making the blades of gas turbines, and the components of jet engines and rocket installations. The most important alloying elements of high-temperature steels are chromium (15-20%), nickel (8-15%), and tungsten. High-temperature steels belong to austenite alloys.

Magnetic steels are used to make permanent magnets and the cores of magnetic devices operating in alternating fields. Permanent magnets are made from high-carbon steels alloyed with chromium or tungsten. They are well magnetized and retain a residual induction for a long time. The cores of magnetic devices are made from low-carbon (less than 0.005% C) alloys of iron with silicon. These steels are readily remagnetized and are characterized by a low value of their electrical losses.

Different systems are used in different countries to designate the various grades of alloy steels. The following letter and number system is used in the USSR. Each alloying element is designated by a Russian letter: H stands for nickel, X for chromium, Γ for manganese, etc. The first numbers in the alloy designation indicate the carbon content in the steel (in hundredths of a per cent). The number following a letter symbol indicates the content of the given element (no number is used if its content is about 1% or less). For example, a steel containing from 0.10 to 0.15% carbon and from 1.3 to 1.7% manganese is designated 12Γ2. The grade designation X18H9 stands for steel containing 18% chromium and 9% nickel. Apart from this system, non-standard symbols are sometimes used.

Commercial iron differs from steel in its properties. It is capable of plastic deformation to a very small extent (in ordinary conditions it does not lend itself to forging) but has good casting properties. Commercial iron is cheaper than steel.

We have already mentioned (p. 350) that in the crystallization of liquid iron, and also in the decomposition of the austenite con-

tained in such phases, the carbon usually separates as cementite. In the conditions considered, however, the cementite is thermodynamically unstable. Its formation is due only to the fact that the seeds of its crystallization form much more readily and require less diffusion changes than the seeds of graphite. Consequently, in conditions of very slow cooling of liquid iron, the carbon may crystallize not as cementite, but as graphite. The formation of graphite is also greatly facilitated in the presence of fine particles of admixtures (especially admixtures of graphite) in the molten iron.

Hence, depending on the conditions of crystallization, iron may contain carbon as cementite, graphite, or their mixture. The shape of the graphite formed may also vary.

White iron contains all its carbon as cementite. It is very hard and brittle, which explains its limited use. It is mainly produced for conversion to steel.

Gray iron contains its carbon chiefly in the form of graphite plates. It has high casting properties (a low crystallization point, fluidity in the liquid state, small shrinkage) and is the main material for castings. It is widely employed in mechanical engineering for casting machine tool beds and mechanisms, pistons, and cylinders. Gray iron always contains other elements in addition to carbon. The most important of them are silicon and manganese. In most grades of gray iron, the carbon content ranges from 2.4 to 3.8%, the silicon content from 1 to 4%, and that of manganese is up to 1.4%.

High-strength iron is produced by adding certain elements to molten iron, particularly magnesium, under whose influence the graphite acquires a spherical shape in crystallization. Spherical graphite improves the mechanical properties of iron. High-strength iron goes to make crankshafts, cylinder lids, components of rolling mills, rolling mill rolls, pumps, and valves.

Malleable iron is produced by prolonged heating of white iron castings. It is used to make components operating under impact and vibration loads (for example, crankcases and motor vehicle rear axles). The plasticity and strength of malleable iron are due to the fact that the carbon is in it as flaky graphite.

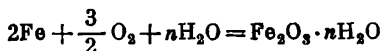
128. Chemical Properties of Iron.

Compounds of Iron

Pure iron is produced in various ways. The most important of them are the thermal decomposition of iron pentacarbonyl (see Sec. 79) and the electrolysis of aqueous solutions of its salts.

Iron rapidly rusts in humid air, i.e. becomes covered with a brown coat of hydrated iron oxide, which owing to its porosity does

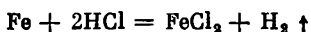
not protect the iron from further oxidation. Iron corrodes intensively in water; with an abundant supply of oxygen, iron(III) oxide hydrates are formed:



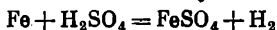
With insufficient oxygen or when its access to the iron is hampered, the mixed oxide Fe_3O_4 ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) is formed:



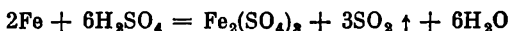
Iron dissolves in hydrochloric acid of any concentration:



It dissolves similarly in dilute sulphuric acid:



In concentrated sulphuric acid solutions, iron is oxidized to iron(III):



But in sulphuric acid whose concentration is close to 100%, iron becomes passive and virtually no reaction occurs.

Iron dissolves in dilute and moderately concentrated solutions of nitric acid:

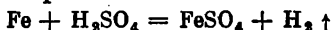


At high concentrations of the HNO_3 , dissolving retards, and the iron becomes passive.

Iron is characterized by two series of compounds: of iron(II) and of iron(III). The former correspond to iron(II) oxide FeO , and the latter to iron(III) oxide Fe_2O_3 . In addition, salts of ferric acid H_2FeO_4 are known in which the oxidation state of iron is +6.

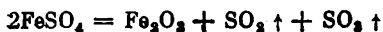
Iron(II) Compounds. Iron(II) salts are formed when iron is dissolved in dilute acids except for nitric acid. The most important of them is iron(II) sulphate or green vitriol $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ forming light green crystals well soluble in water. Iron(II) sulphate gradually effloresces in air and is simultaneously oxidized from its surface, transforming into the yellow-brown basic salt of iron(III).

Iron(II) sulphate is produced by dissolving steel trimmings in 20-30% sulphuric acid:

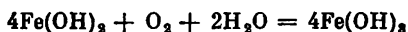


Iron(II) sulphate is used to combat plant pests, in the production of ink and mineral pigments, and in the dyeing of fabrics.

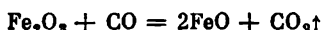
When green vitriol is heated, water is liberated and a white mass of the anhydrous salt FeSO_4 is obtained. At temperatures above 480°C , the anhydrous salt decomposes with the liberation of sulphur dioxide and trioxide; the latter forms a heavy white vapour of sulphuric acid in humid air:



When a solution of an iron(II) salt reacts with an alkali, a white precipitate of iron(II) hydroxide $\text{Fe}(\text{OH})_2$ is formed, which in air owing to oxidation rapidly acquires a greenish, and then a brown colour, transforming into iron(III) hydroxide $\text{Fe}(\text{OH})_3$:

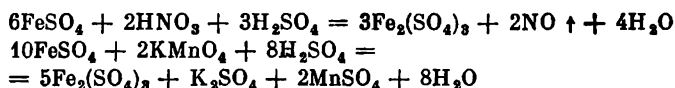


Anhydrous iron(II) oxide FeO can be prepared as a black readily oxidizable powder by reducing iron(III) oxide with carbon monoxide at 500°C :



Alkali metal carbonates precipitate white iron(II) carbonate FeCO_3 from solutions of iron(II) salts. In water containing CO_2 , iron(II) carbonate, like calcium carbonate, partly transforms into the more soluble acid salt $\text{Fe}(\text{HCO}_3)_2$. Iron is contained in natural ferruginous mineral waters in the form of this salt.

Iron(II) salts can readily be transformed into iron(III) salts by reacting them with various oxidizing agents—nitric acid, potassium permanganate, or chlorine, for instance:



Owing to their ability of being readily oxidized, iron(II) salts are often used as reducing agents.

Iron(III) Compounds. *Iron(III) chloride* FeCl_3 forms dark brown crystals with a greenish change of colours. It is highly hygroscopic; absorbing moisture from the air, it transforms into crystal hydrates containing a varying amount of water and deliquescent in air. In this state, iron(III) chloride is brown-orange. In a dilute solution, FeCl_3 hydrolyzes to basic salts. In the vapour state, iron(III) chloride has a structure similar to that of aluminium chloride (p. 305) and corresponding to the formula Fe_2Cl_6 ; appreciable dissociation of Fe_2Cl_6 into FeCl_3 molecules begins at a temperature of about 500°C .

Iron(III) chloride is used as a coagulant in water purification, and as a catalyst in organic syntheses and in the textile industry.

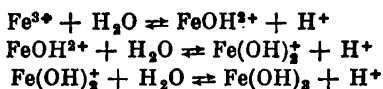
Iron(III) sulphate $\text{Fe}_2(\text{SO}_4)_3$ forms very hygroscopic white crystals that are deliquescent in air. It forms the crystal hydrate $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (yellow crystals). Iron(III) sulphate is greatly hydrolyzed in aqueous solutions. It forms double salts—alums—with alkali metal and ammonium sulphates. An example is ammonium iron alum $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ —light violet crystals well soluble in water. When roasted to above 500°C , iron(III) sulphate decomposes as follows:



Iron(III) sulphate is employed, like FeCl_3 , as a coagulant in water purification, and also for pickling metals. A solution of $\text{Fe}_2(\text{SO}_4)_3$ can dissolve Cu_2S and CuS to form copper(II) sulphate; this property is used in the hydrometallurgical preparation of copper.

When alkalis react with solutions of iron(III) salts, red-brown iron(III) hydroxide $\text{Fe}(\text{OH})_3$ precipitates. It is insoluble in an excess of the alkali.

Iron(III) hydroxide is a weaker base than iron(II) hydroxide. This manifests itself in that iron(III) salts are greatly hydrolyzed, while $\text{Fe}(\text{OH})_3$ forms no salts with weak acids (for instance with carbonic or hydrosulphuric acid). Hydrolysis also explains the colour of solutions of iron(III) salts: notwithstanding the fact that the Fe^{3+} ion is almost colourless, solutions containing it are yellow-brown. The explanation is the presence of hydroxo ions of iron or of $\text{Fe}(\text{OH})_3$ molecules, which form owing to hydrolysis:

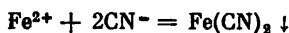


The colour darkens when the solution is heated, while when acids are added it becomes lighter owing to the suppression of hydrolysis.

Iron(III) hydroxide loses water when roasted and transforms into iron(III) oxide Fe_2O_3 . The latter is encountered in nature as hematite (red iron ore) and is used as a brown pigment—Indian red or colcothar.

A characteristic reaction distinguishing iron(III) salts from those of iron(II) is the reaction of potassium thiocyanide KSCN or ammonium thiocyanide NH_4SCN with iron salts. A potassium thiocyanide solution contains colourless SCN^- ions that combine with $\text{Fe}(\text{III})$ ions to form garnet-red, weakly dissociated iron(III) thiocyanide $\text{Fe}(\text{SCN})_3$. When the thiocyanides react with iron(II) ions, the solution remains colourless.

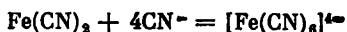
Cyanide Compounds of Iron. The reaction of solutions of iron(II) salts with soluble cyanides, for instance potassium cyanide, yields a white precipitate of iron(II) cyanide:



The precipitate dissolves in excess potassium cyanide owing to the formation of the complex salt $\text{K}_4[\text{Fe}(\text{CN})_6]$ —potassium hexacyanoferrate(II)



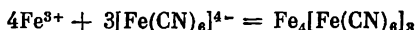
or



Potassium hexacyanoferrate(II) $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ crystallizes as large light yellow prisms. This salt is also known as yellow prussiate

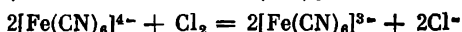
of potash. When dissolved in water, the salt dissociates into potassium ions and the exceedingly stable complex ions $[\text{Fe}(\text{CN})_6]^{4-}$. Such a solution contains virtually no Fe^{2+} ions and gives no reactions characteristic of iron(II).

Potassium hexacyanoferrate(II) is a sensitive reagent for iron(III) ions because the $[\text{Fe}(\text{CN})_6]^{4-}$ ions react with Fe^{3+} ions to form the insoluble (in water) salt iron(III) hexacyanoferrate(II) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, having a characteristic blue colour; this salt is called **Prussian blue**:



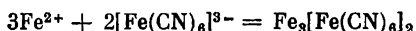
Prussian blue is used as a pigment.

Chlorine or bromine oxidizes the anion of potassium hexacyanoferrate(II) into the ion $[\text{Fe}(\text{CN})_6]^{3-}$:



The salt $\text{K}_3[\text{Fe}(\text{CN})_6]$ corresponding to this anion is called **potassium hexacyanoferrate(III)**, or **red prussiate of potash**. It forms red anhydrous crystals.

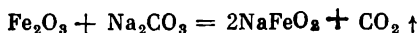
If potassium hexacyanoferrate(III) is reacted with a solution of an iron(II) salt, a precipitate of iron(II) hexacyanoferrate(III) (**Turnbull's blue**) is obtained that greatly resembles Prussian blue, but has a different composition*:



With iron(III) salts, $\text{K}_3[\text{Fe}(\text{CN})_6]$ forms a greenish brown solution.

In most of their other complex compounds, as in the cyanoferrates considered above, the coordination number of iron(II) and iron(III) is six.

Ferrites. When iron(III) oxide is fused with sodium or potassium carbonates, ferrites are formed—salts of **ferrous acid** HFeO_2 that has not been obtained in the free state, for instance sodium ferrite NaFeO_2 :

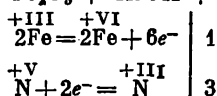
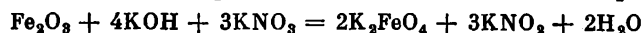


In engineering, the name ferrites or ferrite materials is applied to the products obtained in sintering powders of iron(III) oxide and oxides of some divalent metals, for instance, nickel, zinc, and manganese. Sintering is conducted at 1000 to 1400 °C. Ferrites have valuable magnetic properties and a high electrical resistance, which underlies the small value of the electrical losses in them. Ferrites find broad application in communication equipment, computers, and in automatic and remote control equipment.

Iron(VI) Compounds. If steel filings or iron(III) oxide are heated with potassium nitrate and hydroxide, an alloy is formed contain-

* Data have been obtained lately indicating that Prussian blue and Turnbull's blue are identical.

ing potassium ferrate K_2FeO_4 —a salt of ferric acid H_2FeO_4 :



When the alloy is dissolved in water, a red-violet solution is obtained from which the water-insoluble barium ferrate $BaFeO_4$ can be precipitated by reaction with barium chloride.

All ferrates are very strong oxidizing agents (stronger than permanganates). Ferric acid H_2FeO_4 and its anhydride FeO_3 corresponding to the ferrates have not been obtained in the free state.

Iron Carbonyls. Iron forms volatile compounds with carbon monoxide called iron carbonyls. Iron pentacarbonyl $Fe(CO)_5$ is a pale yellow liquid boiling at $105^\circ C$, insoluble in water, but soluble in many organic solvents. Iron pentacarbonyl is prepared by passing CO over an iron powder at 150 to $200^\circ C$ and a pressure of 10 MPa. The impurities contained in the iron do not enter into a reaction with the CO, and therefore a very pure product is obtained. When heated in a vacuum, iron pentacarbonyl decomposes into iron and CO. This is taken advantage of to produce highly pure powdered iron—carbonyl iron (see Sec. 79).

The nature of the chemical bonds in the $Fe(CO)_5$ molecule is treated on pp. 114 and 115.

129. Cobalt (Cobaltum)

Cobalt is rare in nature: its content in the Earth's crust is about 0.004% (mass). It is most often combined with arsenic as the minerals smaltite $CoAs_2$ and cobaltite or cobalt glance $CoAs$.

Cobalt is a hard, ductile, lustrous metal resembling iron. Like the latter, it has magnetic properties. Water and air do not react with it. Cobalt dissolves in dilute acids with much greater difficulty than iron.

Cobalt finds its main application in alloys used as heat-resistant and high-temperature materials, and for making permanent magnets and cutting tools. The high-temperature and heat-resistant alloy Vitallium contains 65% Co, 28% Cr, 3% W, and 4% Mo. This alloy retains its high strength and does not lend itself to corrosion at temperatures up to $800-850^\circ C$. The hard alloys named stellites containing 40 to 60% Co, 20 to 35% Cr, 5 to 20% W, and 1 to 2% C are used to make cutting tools. Cobalt is also included in the composition of metalloceramic hard alloys—cermets (see p. 331). Cobalt compounds impart a dark blue colour to glass (owing to the formation of cobalt silicate). Such glass ground into a powder is used under the name of "smalt" or "cobalt" as a blue pigment.

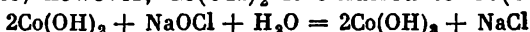
The radioactive isotope ^{60}Co is used in medicine as a source of gamma radiation (a "cobalt gun").

Cobalt forms **cobalt(II) oxide** CoO and **cobalt(III) oxide** Co_2O_3 , and the relevant hydroxides $\text{Co}(\text{OH})_2$ and $\text{Co}(\text{OH})_3$. Two series of salts correspond to these compounds, but those of cobalt(III) are unstable and readily transform into cobalt(II) salts. The mixed oxide Co_3O_4 (or $\text{CoO} \cdot \text{Co}_2\text{O}_3$) is also known.

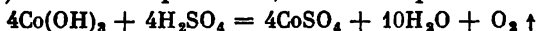
Anhydrous cobalt(II) salts are usually blue, while their aqueous solutions and crystal hydrates are pink. For instance, **cobalt(II) chloride** forms pink crystals of the composition $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Filter paper impregnated with a solution of this salt and then dried can be used as a rough hygroscope (humidity indicator) because depending on the humidity (moisture content) of the air, it acquires various tints from blue to pink.

Cobalt(II) hydroxide $\text{Co}(\text{OH})_2$ is obtained when an alkali is reacted with solutions of cobalt(II) salts. First a precipitate of the blue basic salt appears, which upon boiling of the liquid transforms into the pink hydroxide $\text{Co}(\text{OH})_2$; the latter when roasted produces cobalt(II) oxide CoO of a gray-green colour.

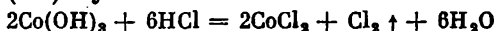
Cobalt(II) compounds are oxidized with greater difficulty than those of iron(II). For instance, cobalt(II) hydroxide is oxidized in air into the dark brown **cobalt(III) hydroxide** $\text{Co}(\text{OH})_3$ at a much slower rate than that of the similar transformation of iron hydroxides. In the presence of strong oxidizing agents, for example sodium hypochlorite, however, $\text{Co}(\text{OH})_2$ is oxidized to $\text{Co}(\text{OH})_3$ rapidly:



When cobalt(III) hydroxide is reacted with oxygen-containing acids, no cobalt(III) salts are formed, but oxygen is liberated and cobalt(II) salts are produced, for example:



Cobalt(III) hydroxide liberates chlorine from hydrogen chloride:



Hence, $\text{Co}(\text{III})$ compounds are less stable than their $\text{Fe}(\text{III})$ counterparts and exhibit a more strongly expressed oxidizing power.

Cobalt(III) is very prone to form complexes. Complex compounds of cobalt(II) are known, but they are very unstable. Cobalt may be either in the cation or in the anion in complex salts. Examples are $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $\text{K}_3[\text{Co}(\text{NO}_2)_6]$. The coordination number of cobalt is six.

130. Nickel [Niccolum]

Like cobalt, nickel occurs in nature chiefly as compounds with arsenic or sulphur. These include the minerals **niccolite** or **arsenical nickel** NiAs and **gersdorffite** NiAsS . Nickel is more abundant than cobalt [about 0.01% (mass) of the Earth's crust].

Tsarist Russia had no nickel industry and imported this metal. The nickel industry was set up only under Soviet power. The first nickel works was run in the Urals in 1934.

Metallic nickel is silvery with a yellowish shade; it is very hard, polishes well, and is attracted by a magnet. It is featured by a high resistance to corrosion—it is stable in the atmosphere, in water, in alkalies, and in a number of acids. Nickel dissolves vigorously in nitric acid. The chemical stability of nickel is due to its disposal to passivation—the forming on its surface of oxide films having a strong protective action.

The bulk of nickel goes to produce a variety of alloys with iron, copper, zinc, and other metals. An addition of nickel in steel increases its toughness and resistance to corrosion. Nickel-based alloys can be grouped into high-temperature, magnetic alloys, and alloys with special properties. High-temperature nickel alloys are employed in modern turbines and jet engines where the temperature reaches 850 to 900 °C. Iron-based alloys do not withstand such temperatures. The most important high-temperature nickel alloys include **nimonic**, **Inconel**, and **Hastelloy**. They contain over 60% nickel, 15 to 20% chromium, and other metals. Metallo-ceramic high-temperature alloys are also manufactured that contain nickel as the binding metal. These alloys withstand heating to 1100 °C. Alloys of the **nichrome** type, the simplest of which contains 80% nickel and 20% chromium, are in great favour for manufacturing the elements of electrical heating appliances.

Special mention among nickel's magnetic alloys must be made of **permalloy**, containing 78.5% nickel and 21.5% iron. It has a very high initial permeability, which underlies its intensive magnetization even in weak fields. Nickel alloys with special properties include **Monel metal**, **nickeline**, **konstantan**, **Invar**, and **platynite**. **Monel metal** (an alloy of nickel with 30% copper) is widely used in chemical engineering because its mechanical properties are superior to those of nickel, while its resistance to corrosion is virtually not inferior to that of nickel. **Nickeline** and **constantan** are also alloys of nickel with copper. They have a high electrical resistance that does not virtually change with the temperature and are used in electrical heating appliances. **Invar** (an alloy containing 36% nickel and 64% iron) does not practically expand when heated to 100 °C and is used in electrical, radio, and chemical engineering. **Platynite**—an alloy of nickel and iron—has the same coefficient of thermal expansion as glass and is used to solder inlets of metal contacts into glass.

Nickel goes in comparatively small amounts to coat other metals. Finely comminuted nickel is a catalyst in many chemical processes. Pure nickel is employed to make laboratory utensils.

Nickel compounds greatly resemble those of cobalt. Like cobalt,

nickel forms nickel(II) oxide NiO and nickel(III) oxide Ni_2O_3 , and the relevant bases. Only one series of nickel salts is known, however, in which it is in the +2 oxidation state.

Nickel(II) hydroxide Ni(OH)_2 forms a light green precipitate when alkalies react with solutions of nickel salts. It loses water when heated and transforms into the gray-green nickel(II) oxide NiO .

Unlike iron(II) and cobalt(II) hydroxides, nickel(II) hydroxide is not oxidized by the oxygen of the air. This displays the higher stability against oxidation of nickel(II) compounds in comparison with their iron and cobalt analogues.

Nickel salts are chiefly green. The greatest use among them is found by nickel sulphate $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ that forms beautiful emerald green crystals.

Nickel(III) hydroxide Ni(OH)_3 is black-brown and is formed when alkalies react with nickel salts in the presence of strong oxidizing agents. It resembles cobalt(III) hydroxide in its properties, but has still more pronounced oxidizing properties.

Nickel(II) forms many complex salts.

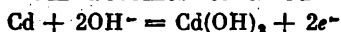
With carbon monoxide, nickel forms the volatile nickel tetracarbonyl Ni(CO)_4 that decomposes when heated with the separation of nickel. The formation and thermal decomposition of nickel carbonyl underly one of the methods of extracting nickel from its ores, and also a process for the production of highly pure nickel.

The most important nickel compound from a practical viewpoint is nickel(III) oxide employed in the manufacture of alkaline cadmium-nickel or iron-nickel accumulators (storage batteries).

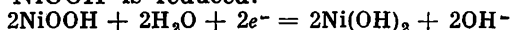
Alkaline Cadmium-Nickel and Iron-Nickel Accumulators. These two kinds of accumulators are very similar. Their main distinction is in the material of the negative electrode plates, which are made from cadmium or iron, respectively. Cadmium-nickel accumulators have found the broadest application.

Alkaline accumulators are mainly produced with lamellar electrodes. The active bodies in them are confined in lamellas—flat small boxes with openings. The active body of the positive plates in a charged accumulator consists chiefly of hydrated nickel(III) oxide $\text{Ni}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or NiOOH . It also contains graphite added to increase the electrical conductance. The active body of the negative plates in cadmium-nickel accumulators consists of a mixture of spongy cadmium and iron powder, and in iron-nickel accumulators of reduced iron powder. A solution of potassium hydroxide containing a small amount of LiOH is the electrolyte.

Let us consider the processes occurring in the operation of a cadmium-nickel accumulator. In the discharge of the accumulator, the cadmium becomes oxidized:

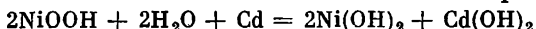


and the NiOOH is reduced:



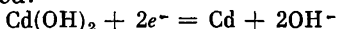
The electrons are carried through the external circuit from the cadmium electrode to the nickel one. The cadmium electrode is the anode and is charged negatively, while the nickel electrode is the cathode and is charged positively.

The net reaction proceeding in a cadmium-nickel accumulator during its operation can be shown by the equation obtained upon summation of the last two electrochemical equations:

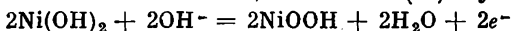


The e.m.f. of a charged cadmium-nickel accumulator is about 1.4 V. In operation of the accumulator (discharge), the voltage across its terminals drops. When it falls to below one volt, the accumulator is charged.

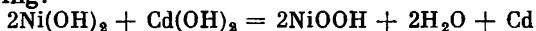
In charging, the electrochemical processes on the accumulator electrodes are "reversed". On the cadmium electrode, the metal is reduced:



and on the nickel electrode, the nickel(II) hydroxide is oxidized:



The net reaction in charging is the opposite of the reaction in discharging:



PLATINUM METALS

131. General

The name **platinum metals** unites the elements of the second and third triads of Group VIII of the periodic table: **ruthenium**, **rhodium**, **palladium**, **osmium**, **iridium**, and **platinum**. These elements form a group of quite rare metals resembling one another in their properties so that their separation involves substantial difficulties.

The platinum metals occur in nature almost exclusively in the native state, generally all together, but they are never encountered in iron ores.

Being greatly dissipated among various rocks, the platinum metals became known to mankind comparatively recently. The existence of platinum was established first, in 1750, before the others. Next, at the beginning of the 19th century, palladium, rhodium, osmium, and iridium were discovered. The last platinum metal—ruthenium—was discovered only in 1844 by K. Klaus, a professor at the Kazan University, who named it ruthenium in honour of Russia (Ruthenia means Russia).

Selected properties of the platinum metals are given in Table 18.

Table 18

Selected Properties of the Platinum Metals

	Ru	Rh	Pd	Os	Ir	Pt
Atomic radius, nm	0.134	0.134	0.137	0.135	0.135	0.138
Ionization energy $E \rightarrow E^+$, eV	7.37	7.46	8.34	8.5	9.1	8.9
$E^+ \rightarrow E^{2+}$, eV	16.8	18.1	19.4	17	17	18.6
Radius of ion E^{2+} , nm	0.085		0.088			0.090
Standard enthalpy of atomization of metal at 25 °C, kJ per mole of atoms	657	556	372	790	669	566
Density, g/cm ³	12.4	12.4	12.0	22.5	22.4	21.5
Melting point, °C	2250	1960	1554	3030	2450	1769
Boiling point, °C	4200	3700	2940	5000	4400	3800

The platinum metals have a low activity and are very stable to chemical action. Some of them do not dissolve not only in acids, but also in aqua regia.

Ruthenium, rhodium, osmium, and iridium are refractory. Notwithstanding their low availability and high cost, these metals together with platinum are finding a variety of technical applications increasing with every passing year.

Although the platinum metals can exhibit different oxidation states in their compounds, especially typical of them are compounds in which their oxidation state is +4. Osmium and ruthenium also form compounds with an oxidation state of these elements of +8.

Osmium(VIII) oxide or osmium tetroxide OsO_4 is the most stable of this element's oxides. It forms slowly even when osmium is kept in air and consists of fusible (melting point 41 °C) pale yellow crystals. The vapour of OsO_4 has a pungent odour and is highly toxic.

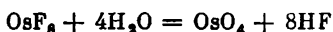
Osmium tetroxide dissolves quite well in water, and its solution does not give an acid reaction with litmus. But, as was first established by L. Chugaev (1918), OsO_4 forms unstable complex compounds with strong alkalis.

Having sharply expressed oxidizing properties, OsO_4 vigorously reacts with organic substances, being reduced to the black osmium dioxide OsO_2 . This underlies the use of OsO_4 for colouring microscopic preparations.

Ruthenium(VIII) oxide, or **ruthenium tetroxide** RuO_4 forms hard golden yellow crystals melting at 25.4°C and soluble in water. Ruthenium tetroxide is considerably less stable than OsO_4 and at a temperature of about 108°C (below its boiling point) it decomposes with an explosion into RuO_2 and oxygen.

Osmium(VIII) fluoride, or **osmium octafluoride** OsF_8 is prepared by directly combining osmium and fluorine at 250°C as a colourless vapour condensing when cooled into lemon-yellow crystals with a melting point of -34.4°C .

Osmium octafluoride has sharply expressed oxidizing properties. Water gradually decomposes it into osmium tetroxide and hydrogen fluoride:



All the platinum metals display a clearly expressed inclination to form complexes.

132. Platinum

Platinum occurs in nature, like gold, in placer deposits as grains always containing admixtures of other platinum metals. The platinum content in the Earth's crust is estimated to be only $5 \times 10^{-8}\%$ (mass).

Platinum is a white lustrous malleable metal that does not change in air even when strongly heated. Individual acids do not react with it. It does dissolve in aqua regia, but much more difficultly than gold.

Owing to the refractoriness and high chemical stability of platinum, it goes to make laboratory utensils: crucibles, bowls, etc.

In the chemical industry, platinum is employed to manufacture corrosion-resistant components of apparatus. Platinum anodes are used in a number of electrochemical production processes (the production of persulphuric acid, perchlorates, and perborates). Platinum has found great favour as a catalyst, especially in conducting oxidation-reduction reactions. It is the first heterogeneous catalyst, known already from the beginning of the 19th century. At present, platinum catalysts are used in the production of sulphuric and nitric acids, in purifying hydrogen from oxygen admixtures, and in a number of other processes. Platinum goes to make the heating elements of electrical furnaces and instruments for measuring temperature (resistance thermometers and thermocouples). In the highly dispersed state, platinum dissolves considerable amounts of hydrogen and oxygen. Its ability to dissolve hydrogen is utilized in the fabrication of hydrogen electrodes (see Vol. 1, p. 294).

In most of its compounds, platinum exhibits oxidation states of $+2$ and $+4$. In both states, it has a clearly expressed ability

of forming complex compounds; of the greatest significance are **platinum(IV)** compounds.

When platinum is dissolved in aqua regia, the product is **hexachloroplatinic** or **chloroplatinic acid** $\text{H}_2[\text{PtCl}_6]$, which upon evaporation of its solution separates as red-brown crystals of the composition $\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$. The potassium salt of this acid is one of the least soluble potassium salts. This is why its formation is used in chemical analysis to detect potassium.

When chloroplatinic acid is heated in a stream of chlorine to 360°C , it decomposes with the liberation of hydrogen chloride and the formation of **platinum(IV) chloride** PtCl_4 .

If an alkali is poured into a solution of $\text{H}_2[\text{PtCl}_6]$, a brown precipitate of $\text{Pt}(\text{OH})_4$ is formed. This substance is known as **platinic acid** because it forms a salt when dissolved in an excess amount of alkali. **Platinum(IV) oxide** PtO_2 is also known.

Platinum(II) chloride PtCl_2 is obtained when chlorine is passed over finely comminuted platinum. It has a greenish colour and is insoluble in water.

The complex compounds of platinum(II) include the salts of **tetracyanoplatinic(II) acid** $\text{H}_2[\text{Pt}(\text{CN})_4]$. The barium salt of this acid $\text{Ba}[\text{Pt}(\text{CN})_4]$ exhibits bright fluorescence when acted upon by ultraviolet and X-rays and is used in fluoroscopy to coat fluorescing screens.

133. Palladium. Iridium

Palladium is a silvery metal, the lightest of the platinum metals, the softest and the most malleable of them. It is remarkable for its ability to absorb an enormous amount of hydrogen (up to 900 volumes per volume of the metal). Upon absorbing hydrogen, palladium retains its metallic appearance, but grows substantially in volume, becomes brittle, and readily forms cracks. The hydrogen absorbed by palladium is evidently in a state approaching the atomic one, and is therefore very active. A palladium plate saturated with hydrogen transforms chlorine, bromine, and iodine into hydrogen halides, reduces iron(III) salts to iron(II) ones, mercury(II) salts to mercury(I) ones, and sulphur dioxide to hydrogen sulphide.

Palladium is used to make some kinds of laboratory utensils, and also components of apparatus for separating hydrogen isotopes. Alloys of palladium with silver are used in communication apparatus, particularly for making contacts. Alloys of palladium with gold, platinum, and rhodium are employed in thermostats and thermocouples. Some palladium alloys are used in jewelry making and in dentistry.

Palladium applied on asbestos, porcelain, or other supports is the catalyst of a number of oxidation-reduction reactions. This

property of it is taken advantage of both in laboratories and at chemical enterprises in the synthesis of some organic compounds. A palladium catalyst is employed to purify hydrogen from traces of oxygen, and also oxygen from traces of hydrogen.

In the chemical respect, palladium differs from the other platinum metals by its high activity. When heated to redness, it combines with oxygen to form the oxide PdO , dissolves in nitric acid, hot concentrated sulphuric acid, and in aqua regia.

Like platinum, palladium is characterized by the +2 and +4 oxidation states; the compounds of palladium(II) are more stable. Most palladium salts dissolve in water and are greatly hydrolyzed in solutions. Palladium(II) chloride PdCl_2 is very readily reduced in a solution to the metal by some gaseous reducing agents, particularly by carbon monoxide. This underlies its use for detecting carbon monoxide in gas mixtures. It is also employed as a catalyst of some oxidation-reduction reactions.

Iridium differs from platinum in its very high melting point and in its still greater stability to various chemical actions. Neither individual acids nor aqua regia react with iridium. It is also considerably superior to platinum in its hardness.

Pure iridium and an alloy consisting of 90% platinum and 10% iridium are used to make certain scientific instruments. The international standards of the metre and kilogram are made from this alloy.

Andrianov, K. A., 188, 189
Anosov, P. P., 345, 352

Bagration, P. R., 249
Baikov, A. A., 352
Bardin, I. P., 352
Bazarov, A. I., 112
Berthelot, M. P. E., 121
Berzelius, J. J., 120, 121
Bessemer, H., 354
Boussingault, J. B., 87
Butlerov, A. M., 121, 123, 140, 276

Cavendish, H., 9
Chernov, D. K., 345
Chernyaev, I. I., 275
Chugaev L. A., 257f, 372

Davy, H., 230

Engels, F., 121

Favorsky, A. E., 144
Fersman, A. E., 23

Glauber, J. R., 57
Grinberg, A. A., 275, 276

Janssen, P. J., 341

Kazansky, B. A., 145
Kekule, F. A., 145
Kirchhoff, K. S., 164
Klaus, K. K., 371
Kolbe, H., 121
Kossel, W., 263
Kuchеров, M. G., 156
Kurnakov, N. S., 223

Lavoisier, A. K., 9, 43
Lebedev, S. V., 174
Le Chatelier, H. L., 345
Liebig, J., 87
Lockyer, J. N., 341
Lomonosov, M. V., 83
Lovits, T. E., 107

Magnus A., 263
Markovnikov, V. V., 123, 144
Martin, P., 354
Mendeleev, D. I., 120, 190, 337
Morozov, N. A., 340

Nekrasov, B. V., 276

Osmond, F., 345

- Paracelsus, P., 9
Pavlov, M. A., 352
Perey, M., 232
Pisarzhevsky, L. V., 61
Platé, A. F., 145
Priestly, J., 43
Pryanishnikov, D. N., 87

Ramsay, W., 339, 341
Rayleigh, Lord (J. W. Strutt), 339

Scheele, K. W., 25, 43, 330

Werner, A., 251f, 254, 261, 262
Winkler, C. A., 190
Wöhler, F., 121, 304

Zelinsky, N. D., 145
Zinin, N. N., 167, 168

SUBJECT INDEX

- Accumulator(s),**
 alkaline, 370f
 cadmium-nickel, 370f
 iron-nickel, 370
 lead, 197f
 silver-zinc, 246
- Acetaldehyde, 154, 156**
- Acetic acid, 155, 157**
- Acetic aldehyde, 154, 155f**
- Acetone, 154, 156**
- Acetyl cellulose, 166**
- Acetylene, 127, 141, 143**
 series, 127, 141
- Acid(s),**
 dibasic, 137
 heteropoly, 259
 higher fatty, 158
 isopoly, 258f
 organic, 136f
 anhydrides, 136
 chloride, 136
- Acidocomplexes, 256**
- Actinides, 310, 314ff**
- Actinium, 310f**
- Agate, 181**
- Agent(s),**
 antiknocking, 140f
 bleaching, 17, 26, 34, 325
 complexing, 252
 charge, 255
 dehydrating, 91
 deoxidizing, 355
 gas drying, 56
 heat-carrying, 99
 oxidizing, 17, 47, 80, 83, 197, 235,
 328, 335, 338f
 properties and medium, 96f
 reducing, 51, 54, 233
 properties and medium, 96f
- Agrochemistry, 87**
- Air,**
 composition, 42f, 67, 339
 dust in, 42
 liquid, 43
 mass, 42
- Alanine, 168**
- Alcohol(s), 150ff**
 amino, 137
 diatomic, 137
 hydrolysis, 152
 monatomic, 153
 polyatomic, 153
 wood, 152
- Alcoholates, 150**
- Alkanes, 137ff, *see also* Hydrocarbons, saturated**
- Alkenes, 141, *see also* Hydrocarbons, unsaturated**
- Alkyl radical, 138**
- Alkynes, 141, *see also* Series, acetylene**
- Alloy(s), 211f**
 aluminium, 307
 composition-property diagrams, 222f
 cooling curves, 213f
 copper, 241
 corrosion-resistant, 246, 279, 291, 295
 eutectic composition, 215
 fusible, 99, 295
 heat-resistant, 224, 313, 320, 324,
 332f, 337, 367
 iron, 344, 359ff, *see also* Steel(s)
 lead, 195
 light-weight, 282, 321
 nickel, 369
 magnetic, 369
 phase diagrams, 212ff, 345ff
 structure, 216
 tin, 191
 tool, 333, 367

- Alpha-stannic acid, 193
 Alum(s), 58, 308
 ammonium iron, 364
 chrome, 326, 329
 potassium, 58
 Alumina, 304, 307
 Aluminates, 306, 308
 Aluminium, 299, 304ff
 alloys, 307
 bronzes, 241
 carbide, 107
 chloride, 308
 hydride, 305f
 hydroxide, 308
 oxide, 307
 production, 304f
 sulphate, 308
 Aluminizing, 224, 307
 Aluminosilicates, 177, 183, 184
 Aluminothermics, 209
 Alunite, 304
 Amalgams, 296
 Americium, 314
 Amethyst, 181
 Amides, metal, 69f
 Aminates, 255
 Amines, 136, 166f
 Amino acids, 137, 168
 Ammines, 255
 Ammonals, 73
 Ammonia, 68ff
 oxidation, 85f
 preparation, 68, 69, 71, 73
 spirit, 69
 synthesis from hydrogen and nitro-
 gen, 75f
 Ammonium, 71
 chloride, 71, 72, 73
 hydroxide, 71
 ion, 71
 hydrolysis, 71f
 test for, 72
 molybdate, 331f
 nitrate, 72f
 nitrite, 67
 sulphate, 72
 tetrachlorozincate, 294
 Ammophos, 94
 Amyloid, 165
 Analysis,
 luminescence, 294
 physicochemical, 223
 Anid, 176
 Anhydrite, 58
 Aniline, 167
 Anions, complex, 245, 250
 Anthracene, 145
 Anthracite, 117, 118
 Antifreezes, 153
 Antimonates, 99
 Antimonic acid, 99
 Antimonides, 98
 Antimonite, 98
 Antimonous acid, 98f
 Antimony, 66, 98
 hydride, 98
 sulphides, 99
 Antimony(III),
 hydroxide, 99
 oxychloride, 99
 Antimonyl, 99
 chloride, 99
 Apatite, 87
 Aqua regia, 84
 Aquacomplexes, 255f, 274
 and water of crystallization, 256
 Argentite, 245
 Argon, 339f, 342
 Arsenates, 96
 Arsenic, 66, 94ff
 acid, 96
 allotropic modifications, 94f
 detection, 95
 sulphides, 97
 trihydride, 95
 white, 95
 Arsenic(III) hydroxide, 95
 Arsenides, 95
 Arsenites, 96
 Arsenopyrite, 94
 Arsenous acid, 95
 Arsine, 95
 Asbestos, 183, 184, 283f
 Astatine, 181, 20
 Atom(s),
 asymmetrical, 131f
 bridge, 281, 302, 305
 central, 252
 mutual influence in organic mole-
 cules, 133f
 radii, 313
 structure in metals, 200ff
 Auric acid, 250
 Austenite, 347, 357f
 Autoxidation-autoreduction, 17
 Azides, 77
 Band,
 conduction, 201ff
 energy, 201f
 forbidden, 203f
 valence, 201ff
 Barite, 288
 Barium, 277f, 288f
 carbonate, 289

- Barium
 ferrate, 367
 hydroxide, 289
 oxide, 289
 peroxide, 289
 sulphate, 57, 289
 tetracyanoplatinate(II), 374
 titanate, 321
- Bauxite, 304
- Bearings, porous, 331
- Bed, fluidized, 290f
- Benzene, 144f
 molecule, segment model, 149
 properties, 146
 structure, 147f
- Benzoic acid, 158
- Benzyl alcohol, 150
- Berkelium, 314
- Beryl, 279
- Beryllium, 277f
 chloride, 280f
 hydroxide, 280, 281f
 oxide, 281
- Beta-stannic acid, 192, 193f
- Bidentates, 254
- Bismite, 99
- Bismuth, 66, 99f
 glance, 99
 hydride, 100
 ochre, 99
- Bismuth(III),
 chloride, 100
 hydroxide, 100
 nitrate, 100
 oxide, 100
 sulphide, 100
- Bismuthates, 100
- Bismuthine, 100
- Bismuthinite, 99
- Bismuthyl, 100
- Blast furnace,
 design, 352
 operation, 352f
- Bond(s),
 carbon atoms, in benzene ring, 147f
 donor-acceptor, 113, 256, 267f
 double, 127, 128
 ionogenous, 252
 metallic, 203
 multiple, 127, 128f
 strength, 130
 transition to single bonds, 129
 non-ionogenous, 252
 in organic compounds, 122
 pi, 128f
 pi-dative, 270
 sigma, 128f
 single, 127
- Bond(s),
 strength, 20f
 three-centre, 47, 53, 302
 triple, 127, 128f
 formation, 112f
- Boneblack, 107
- Boranes, 301f
- Borates, 303
- Borax, 300, 303
- Boric acid, 303
- Boric anhydride, 303
- Borides, 301
- Boriding, 300
- Boron, 299ff
 carbide, 301
 halides, 301
- Brasses, 241
- Brimstone, 48
- Bromic acid, 38
- Bromides, 32
- Bromine, 18f, 20ff, 26, 27, *see also*
 Halogen(s)
 chemical activity, 23f
 oxygen-containing compounds, 38
- Bromobenzene, 146
- Bronzes, 241, 295
- Brownite, 334
- Butadiene, 141, 142
- Butylenes, 131
- Cadmium, 289f, 295
 bronzes, 295
 hydroxide, 295
 sulphide, 295
- Calcium, 277f, 284ff
 carbide, 107, 143
 carbonate, 110, 284
 dissociation pressure, 285
 chloride, 31
 cyanamide, 74f
 hydride, 278, 284
 hydrogen carbonate, 110, 286
 hydroxide, 285f
 nitrate, 85
 nitride, 69
 oxide, 285
 plumbate, 197
 sulphate, 57
- Californium, 314
- Calomel, 297
- Calorizing, 307
- Caoutchoucs, 173
 natural, 173
- Capron, 176
- Carat, 246
- Carbamide, 112, 121
- Carbides, 107f, 333, 360
 double, 360

- Carbine, 103
- Carbohydrates, 161ff
- Carbolic acid, 153, *see also* Phenol(s)
- Carbon, 101ff
 - activated, 106f
 - allotropy, 103
 - amorphous, 106f
 - black, 107
 - bonds between atoms, 127ff
 - chains, 125
 - branched, 130f
 - structure, 126f
 - unbranched, 130f
 - chemical properties, 107
 - compounds, diversity, 102
 - covalence, 123
 - dioxide, 107, 108f
 - formation in nature, 42
 - disulphide, 115
 - electron configuration, 123
 - monoxide, 107, 112ff
 - structure of molecule, 112f
 - triple bond formation, 112f
 - structure, 123
 - tetrachloride, 150
 - valence angles, 124
- Carbonates, 109f
 - migration in nature, 110
- Carbonic acid, 109
 - dissociation constants, 109
 - salts, 109
- Carbonyls, metal, 114
- Carborundum, 179
- Carboxylic acids, 136, 157ff
- Carnallite, 20, 238, 282
- Carnotite, 315
- Cassiterite, 191
- Catalyst(s), 75, 296, 298, 337, 373, 374f
 - Phillips, 171
 - supports, 184
 - Ziegler, 171
- Celestite, 288
- Cell(s),
 - air-zinc, 292f
 - dry, 292
 - galvanic, 291ff
 - manganese-zinc, 291f
 - oxidation-reduction reaction, 292f
- Cellulose, 164, 165f
 - acetates, 166
 - nitrates, 165f
 - processing into fibre, 166
 - saccharization, 152
 - separation from wood, 165
 - sulphite, 165
- Cement, 59, 187f
 - acid-resistant, 188
- Cement,
 - alumina, 188
 - mortar, 188
 - setting, 187
 - silicate, 187
- Cementite, 347, 357, 362
- Ceramics, 186f
- Cerium, 311
- Cermets, 331
- Cesium, 230, 232f
- Chalcocite, 240
- Chalcopyrite, 240
- Chalk, 110, 284
- Chalybite, 111
- Charcoal, 106, 118
 - bone, 107
- Chemistry,
 - crystal, 251
 - organic, 123
- Chlorates, 35
- Chloric acid, 35, 36
- Chlorides, 31
- Chlorin, 172
- Chlorine, 18ff, 25ff, *see also* Halogen(s)
 - chemical activity, 23
 - dioxide, 36
 - hydrolysis, 33
 - oxide, 35
 - oxyacids, 33ff
 - oxygen-containing compounds, 33
- Chlorites, 36
- Chloroauric acid, 250
- Chloroform, 150
- Chlorophyll, 258, 284
- Chloroplatinic acid, 374
- Chlorostannic acid, 193
- Chlorous acid, 36
- Chromates, 327f
- Chrome green, 326
- Chrome yellow, 327
- Chromic acid, 327
- Chromic anhydride, 326, 327, 329
- Chromite, 325
- Chromites, 326
- Chromium, 325ff
 - trioxide, 327, 329
- Chromium(II),
 - chloride, 326
 - hydroxide, 326
 - oxide, 326
- Chromium(III)
 - chloride, crystal hydrates, 327
 - hydroxide, 326
 - oxide, 326
- Chromium(VI) oxide, 326
- Cinnabar, 296
- Cis-isomer, 261f

- Coal, 116f
 - bituminous, 117, 118
 - brown, 117, 118
 - hard, 117
 - soft, 117
 - underground gasification, 120
- Cobalt, 342f, 367f
 - glance, 367
- Cobalt(II),
 - chloride, 368
 - hydroxide, 368
 - oxide, 368
- Cobalt(III),
 - hydroxide, 368
 - oxide, 368
- Cobaltite, 367
- Coke, 106
 - peat, 117
- Colcothar, 365
- Combustion, 44
- Complex compounds, 243ff, 247f, 251ff, 281, 368, 374
 - acid and basic properties, 274f
 - amphoteric, 274
 - basic types, 255ff
 - chelate, 256f
 - in nature, 258
 - chemical bond, 263f
 - cluster, 258
 - coordination formulas, 252ff
 - confirmation,
 - by exchange reactions, 253
 - by molar conductivity, 253f
 - by X-ray structural method, 254
 - cyclic, 256
 - dissociation,
 - primary, 270
 - secondary, 270f
 - stepped, 272
 - explanation of colour, 267
 - high-spin paramagnetic, 266
 - inner coordination sphere, 252
 - low-spin diamagnetic, 266
 - and molecular orbital method, 270
 - molecular orbitals, 270
 - mononuclear, 258
 - nomenclature, 259f
 - outer coordination sphere, 252
 - polynuclear, 258
 - with bridge atoms, 258
 - sandwich, 267
 - stability in solutions, 270ff
 - structure, 263f
 - spatial, 261ff
 - transition series, 256
 - and valence bond method, 267ff
- Complexes, *see* Complex compounds
- Complexons, 256f
- Compound(s),
 - amphoteric, 38, 168, 190, 192, 196, 197, 280, 281f, 293, 308, 316, 326
 - clathrate, 21, 340f
 - complex, *see* Complex compounds
 - coordination, 253
 - coordinationally saturated, 254
 - cyclic, 127
 - high-molecular, 169ff
 - inclusion, 340
 - intermetallic, 220
 - intracomplex, 256
 - organic, *see* Hydrocarbons, Organic compounds
 - organoelement, 121, 136
 - organometallic, 136, 141
 - organosilicon, 137, 188f
 - tautomeric forms, 163
 - varying composition, 52
- Concrete, 188
- Constantan, 241, 369
- Contraction, lanthanide, 312
- Converter, 354
- Copel, 241
- Copolymerization, 174f
- Copper, 238ff
 - alloys, 241
 - complex compounds, 243ff
 - glance, 48, 240
 - pyrite, 240
 - sulphate, 58
- Copper(I),
 - chloride, 242
 - oxide, 242
- Copper(II),
 - acetate, 243
 - acetate-arsenate, 243
 - carbonate hydroxide, 243
 - chloride, 243
 - hydroxide, 242f
 - nitrate, 243
 - oxide, 242
 - sulphate, 243
- Corrosion, 223ff
 - atmospheric, 226
 - contact, 227
 - electrochemical, 224f
 - prevention, 228f
 - gas, 224
 - hydrogen, 11
 - influence of inclusions, 225f
 - inhibitors, 228
 - local, 227
 - in non-uniform aeration, 227
 - in soil, 226f
- Corrosive sublimate, 31, 298

- Corundum, 307
 Cracking, 142
 catalytic, 142
 thermal, 142
 Cryolite, 19, 304
 Crystal(s),
 lattices, 204f
 plastic shear, 206f
 strength, 207
 structure, 204f
 Crystallites, 201
 Cuprite, 242
 Cuprites, 245
 Cupronickels, 241
 Curium, 314
 Curves,
 cooling, 212f
 alloy, 213f
 pure metal, 213
 Cyanides, 116
 Cycloalkanes, 144
 Cyclobutane, 131
 Cycloparaffins, 144

 Dacron, 176
 Dehydrogenation, 141f, 156
 Demercurizers, 296
 Desiccants, 31, 182, 284
 Deuterium, 9
 Dextrin, 165
 Diagrams,
 equilibrium, 212
 phase, *see* Phase diagram(s)
 Diamond, 102, 103
 structure, 103f
 synthetic, 103f
 transformation to graphite, 104, 106
 Diantimony,
 pentoxide, 89
 trioxide, 98
 Diarsenic,
 pentasulphate, 97
 pentoxide, 96
 trioxide, 95, 97
 trisulphide, 97
 Diatomite, 181
 Diborane, 302
 Diboron trioxide, 303
 Dichloride heptoxide, 36
 Dichloroethylene, geometric isomers,
 133
 Dichloromethane, 150
 Dichromates, 327f
 Dichromic acid, 327
 Dicyanogen, 115f
 Dielectrics, 203
 energy bands, 203

 Dienes, 141
 Diethyl ether, 154
 Diethylenes, 141
 Dihydrogen,
 arsenates, 96
 phosphates, 91
 Diiodine pentoxide, 38
 Diketones, 137
 Dimers, 305
 Dimethyl amine, 166
 Dimethyl ketone, 154, 15
 Dinitrogen,
 oxide, 77f
 pentoxide, 81
 tetroxide, 80
 trioxide, 81
 Diolefins, 141
 Diphosphates, 92
 Diphosphoric acid, 92
 Diphosphorus,
 pentoxide, 91
 trioxide, 90f
 Disaccharides, 163
 Disilane, 180
 Disinfectants, 17, 26, 31, 47, 53,
 156, 248, 303
 Disulphates, 58
 Disulphuric acid, 58
 Diuranates, 316
 Diuranic acid, 316
 Divinyl, 141
 Dolomite, 282
 Dry-bone ore, 290
 Duality,
 chemical, 12
 oxidation-reduction, 16, 79, 82
 Duralumins, 307
 Dust, in air, 42
 Dysprosium, 312

 Ebonite, 50
 Einsteinium, 314
 Electrolysis, diaphragm method, 236
 Electrolyzer, 304
 with diaphragm, 236
 Elektrons, 282
 Elements,
 alloying, 360f
 d, 238
 f, 314
 transition, 317ff
 Enant, 176
 Enantiomers, 132
 Energy, crystal-field splitting, 265
 Enzymes, 121
 Epsom salt, 283
 Erbium, 312

- Erosion, 183
- Esters, 136, 151, 159f
 - hydrolysis, 159f
- Ethane, 125, 128
- Ethanol, 150, 152
- Ethers, 136, 154
- Ethyl alcohol, 150, 152
 - dissociation constant, 151
 - production, 152f
- Ethyl formate, 159
- Ethyl radical, 138
- Ethylbenzene, 144f
- Ethylene, 127, 141, 142, 143
 - glycol, 153
 - molecule,
 - spatial models, 130
 - structure, 128, 129
 - series, 127, 141
- Europium, 311
- Eutectic, 215
- Eutectoid, 349
- Exchange, cation, 288
- Exchanger,
 - anion, 288
 - cation, 288
- Explosives, 73, 147, 153

- Family, iron, 343
- Fats, 160f
 - hydrogenation, 160
 - hydrolysis, 160
- Feldspars, 183
- Fermium, 314
- Ferrates, 367
- Ferric acid, 363, 367
- Ferrite(s), 347, 357, 366
- Ferrites, 311
- Ferrochrome, 325
- Ferrotitanium, 321
- Ferrous acid, 366
- Ferrovandium, 323
- Fertilizer(s), 31, 72f, 74, 75, 84, 85,
 - 87, 93f, 112, 237f, 303
 - compound, 94
 - mineral, 93
 - mixed, 94
 - organic, 93
 - single, 94
- Fibre(s),
 - acetate, 166
 - artificial, 166, 177
 - chemical, 177
 - natural, 177
 - synthetic, 177
 - viscose, 166
- Filters, metallic, 331
- Firedamp, 138

- Firewood, 117
- Flasks, Dewar, 42f
- Flint, 181
- Fluorapatite, 19
- Fluorides, 30
- Fluorine, 18f, 25f, *see also* Halogen(s)
 - anomalous properties, 21
 - chemical activity, 23
 - oxidizing properties, 24
 - oxygen-containing compounds, 33
- Fluoroberyllates, 281
- Fluoroplast, 172
- Fluorspar, 19
- Fluosilicates, 180
- Fluosilicic acid, 30, 180
- Flux(es), 208, 353
 - soldering, 73, 294
- Formaldehyde, 154
- Formalin, 156
- Formic acid, 114, 157
 - salts, 114
- Formula(s),
 - Kekule's, 145, 147, 149
 - perspective, 162f
- Francium, 230, 232
- Freons, 26, 150
- Fructose, 161, 162
- Fuel, 116f
 - engine, antiknocking properties, 140
 - gaseous, 118f
 - heating value, 118
 - solid, gasification, 119
- Fungicides, 150

- Gadolinium, 311
- Galenite, 194
- Gallium, 299, 309
- Gas(es),
 - adsorption by charcoal, 106
 - coke, 119f
 - complex, 119
 - detonating, 13
 - electron, 203
 - generator, Kipp, 10, 11
 - inert, *see* Gas(es), noble
 - marsh, 137
 - mine, 137
 - mixed, 119
 - natural, 118, 137
 - noble, 339f
 - compounds, 340f
 - producer, 119
 - straight, 119
 - water, 119
- Germanates, 190

- Germanium, 101, 190f, 210
 dioxide, 190
 hydrides, 190
 tetrahydride, 190
Gersdorffite, 368
Glass, 184f, 313
 coloured, 295, 314, 326, 367
 crystal, 185
 fibre, 185
 laminates, 186
 flint, 185
 organic, 173
 production, 184f
 properties, 185
 quartz, 185
 refractory, 185, 322
 soluble, 182
 special, 191, 196, 303, 322
 structure, 184
 water, 182
 window, 184
Glass-ceramics, 186
Glauber's salt, 57
Glaze, 187
Glucose, 152, 161f
 alpha-form, 162f
 beta-form, 162f
 production, 164
 straight-chain form, 162f
Glycerine, 153
Glycine, 168
Gneisses, 183
Gold, 238f, 249f
 amalgam, 296
 chlorides, 250
 compounds, 249f
 oxides, 249, 250
Grains, 205
Granites, 183
Graphite, 102, 104f
 anisotropy, 104
 artificial, 105
 in iron, 362
 structure, 104, 105
Group(s),
 aldehyde, 154f
 amide, 169, 176
 amino, 136
 carbonyl, 136, 154
 carboxyl, 136, 157
 characteristic, 135
 functional, 135, 154, *see also*
 Group(s)
 mercapto, 136
 nitro, 136
 peptide, 169
 sulphydryl, 136
 sulpho, 136
Gutta-percha, 173
Gypsum, 57f, 59, 284
Hafnium, 319, 322
Hallmarks, 246
Halogen(s), 18ff
 chemical properties, 22ff
 electron configuration, 18
 elementary substances, 20
 molecules, 20f
 bond strength, 20f
 oxidizing properties, 22, 24f
 oxygen compounds, 33ff
 physical properties, 18ff
 preparation, 25
 uses, 26f
Hastelloy, 369
Hausmanite, 334
Helium, 339ff
 discovery, 341
Hematite, 343, 365
Hemoglobin, 258
Herbicides, 112
Heteroatoms, 135
Hexachloroplatinic acid, 374
Holmium, 312
Homologues, 126
Hormones, 121
Hydrates,
 crystal, 237, 327
 isomeric salt, 327
Hydrazine, 76
Hydrazoic acid, 77
Hydrides, 12
 metal-like, 12
 organic, 12
 salt-like, 12
Hydrocarbons, 135, *see also* Organic
 compounds
 acyclic, aromatization, 145f
 aromatic, 144ff
 general formula, 144
 multinuclear, 145
 cyclic, 131
 derivatives, 135
 halogen derivatives, 135, 138, 149f
 isostructure, 131
 normal structure, 130f
 pyrolysis, 143
 radicals, 135
 saturated, 126, 137ff
 cyclic, 144
 isomers, 139f
 series, 138f
 unsaturated, 127, 141ff
 general formula, 141
 series, 141

- Hydrochloric acid, 30f
 Hydrocyanic acid, 116
 Hydrofluoric acid, 29f
 Hydrogen, 9ff
 arsenates, 96
 atomic, 14
 borides, 301f
 bromide, 27f, 32
 reducing properties, 32
 carbonates, 109f
 chemical duality, 12
 chloride, 27f
 manufacture, 30f
 combustion, 13
 cyanide, 115f
 difluoride ion, 29
 fluoride, 27ff
 dissociation, 29
 storage, 30
 halides, 27ff
 solubility, 28
 iodide, 27f, 32
 decomposition, 24, 28
 reducing properties, 32
 isotopes, 9
 molecule, 9
 occurrence, 9f
 peroxide, 14ff
 decomposition, 14f, 17
 oxidation-reduction duality, 16
 salts, 16
 structure, 15
 phosphates, 91
 hydrolysis, 91
 phosphide, 90
 production, 10
 industrial, 10
 laboratory, 11
 properties, 9, 11ff
 selenide, 64
 steel corrosion, 11
 sulphates, 57
 sulphide, 50
 water, 50f
 sulphites, 54
 telluride, 64
 uses, 13f
 Hydrogenation, 14
 Hydrolysis, 15, 52, 91, 152, 159f, 235, 365
 Hydroxide, properties,
 and ionic radius, 37f
 and oxidation number, 37
 Hydroxoaluminates, 306, 308
 Hydroxoberyllates, 279, 281
 Hydroxocomplexes, 256
 Hydroxoplumbates, 195
 Hydroxostannates, 193
 Hydroxostannites, 192
 Hydroxozincates, 293
 Hydroxylamine, 77
 Hypobromous acid, 38
 Hypochlorites, 33f
 Hypochlorous acid, 33ff
 Hypochlorous anhydride, 35
 Hypoiodous acid, 38

 Ice, dry, 108
 Ilmenite, 320
 Inconel, 369
 Indian red, 365
 Indium, 299, 309, 343, 371ff
 Infusorian earth, 181
 Insecticides, 89, 97, 150, 180
 Intra-salts, 168
 Invar, 369
 Iodic acid, 38
 Iodic anhydride, 38
 Iodides, 32
 Iodine, 18f, 20ff, *see also* Halogen(s)
 chemical activity, 23f
 oxygen-containing compounds, 38
 tincture, 27
 Ion(s),
 bipolar, 168
 central, 252
 properties and complexing, 275
 complex, 243, 244f, 247, 251
 charge, 255
 instability constant, 271ff
 stability constant, 272f
 Iridium, 371ff, 375
 Iron(s), 342ff
 alloying elements, 352
 alloys, 359ff, *see also* Alloys
 alpha-, 346
 beta-, 346
 blast-furnace, 352
 carbide, 347
 carbonyls, 367
 chemical properties, 362ff
 commercial, 350, 361f
 cooling curve, 346
 crystalline modifications, 346
 cyanide compounds, 365f
 delta-, 346
 electron configuration, 115
 family, 343
 gamma-, 346
 Gibbs energy and temperature, 346
 gray, 362
 high-strength, 362
 malleable, 362
 occurrence, 343f

- Iron(s),
 ore,
 brown, 343
 red, 343
 spathic, 343
 pentacarbonyl, 114f, 211, 367
 physical properties, 345ff
 pig, 352
 conversion into steel, 354f
 production, 344f, 351
 pyrites, 48, 52, 53, 343f
 refining, 211
 spathic, 111
 white, 362
- Iron(II),
 carbonate, 364
 cyanide, 365
 hexacyanoferrate(II), 366
 hydroxide, 364
 oxide, 363, 364
 sulphate, 363
- Iron(III),
 chloride, 364
 hexacyanoferrate(III), 366
 hydroxide, 365
 oxide, 363, 365
- Iron(VI) compounds, 366f
- Isobutylene, 131
- Isomerism, 121f
 cis-trans-, 132f
 coordination, 263
 hydrate, 262, 327
 ionization, 262
 mirror, 262
 optical, 262
 organic compounds, 130ff
 spatial, 131
- Isomers, 139f
 cis-, 133
 geometric, 133
 hydrate, 327
 optical, 132
 trans-, 133
- Isopentanes, 131
- Isoprene, 141, 142, 173
- Jasper, 181
- Kainite, 282
- Kaolin, 183
- Kerosenes, 139
- Ketones, 136, 154, 155f
- Khladons, 26
- Knocking, engine fuel, 140
- Krypton, 339f, 342
 fluorides, 341
- Kurchatovium, 319
- Lactic acid, 132, 158
 enantiomers, 132
 tetrahedral models, 132
- Lanthanides, 310, 311ff
- Lanthanum, 310f
- Lavsan, 176
- Lawrencium, 314
- Lead, 101, 194ff
 alloys, 195
 chromate, 327
 dioxide, 197
 glance, 48, 194
 red, 197
 sugar, 196
 sulphate, 57
 tetraethyl, 140f
- Lead(II),
 acetate, 196
 chloride, 196
 hydroxide, 196
 iodide, 196
 oxide, 196
 sulphate, 196
 sulphide, 196
- Lead(IV) compounds, 197
- Ligand(s), 252, 254
 cis-influence, 276
 mutual influence, 275
 pi acceptor, 270
 properties and coordination, 274
 trans-influence, 275f
- Lignite, 117
- Lime,
 burnt, 285
 chloride, 34
 chlorinated, 34f
 slaked, 285f
 unslaked, 285
 water, 110, 285f
- Limestone, 110, 284
- Limonite, 343
- Litharge, 196
- Lithium, 230ff
- Luminescence, 294
- Luminophors, 294
- Lunar caustic, 247
- Lutetium, 312
- Magnaliums, 307
- Magnesia,
 alba, 283
 cement, 283
 usta, 283
- Magnesite, 110, 282
- Magnesium, 277f, 282ff
 carbonate, 110, 283
 chloride, 283

- Magnesium**,
 hydroxide, 283
 nitride, 69
 oxide, 283
 silicates, 283f
 silicide, 179
 sulphate, 57, 283
Magnetite, 343f
Malachite, 109, 240, 243
Malt, 152
Manganese, 333ff
 dioxide, 335
 oxides, 334f
Manganese(II),
 chloride, 335
 hydroxide, 335
 salts, 335
Manganese(IV) salts, 335
Manganese(VII) oxide, 337
Manganic acid, 335
Manganin, 241, 334
Marble, 110, 284
Margarine, 160
Marls, 187
Martensite, 358
Matches, 36, 89, 99
Materials, photographic, 248
Mendelevium, 314
Mercury, 289f, 295ff
Mercury(I),
 chloride, 297
 nitrate, 297
 oxide, 297
Mercury(II),
 chloride, 31, 298
 iodide, 298
 nitrate, 298
 oxide, 297
 sulphide, 298
Metaaluminates, 308
Metaaluminic acid, 308
Metaarsenous acid, 95
Metachromous acid, 326
Metal(s), 199ff
 alkali, 230ff
 detection, 233
 hydrides, 233
 alkaline earth, 278f
 cathode protection, 229
 chemical properties, 200
 cooling curves, 213
 corrosion, *see* Corrosion
 crystal lattices, 204f
 unit cells, 204
 crystalline structure, 204ff
 ductility, 199, 203
 electrical resistivity, 199
 extraction from ores, 207ff
Metal(s),
 ferrous, 344
 highly pure, 210
 mechanical properties and dislo-
 cations, 206f
 native, 207f
 passive to corrosion, 226
 phase diagrams, 212ff, *see also*
 Phase diagram(s)
 physical properties, 199
 platinum, 343, 371ff
 polycrystalline structure, 205
 protective coatings, 228
 protectors, 229
 rare-earth, 310
 refining,
 carbonyl process, 211
 by electron-beam melting,
 330f
 iodide process, 211
 in vacuum, 210
 refractory, 323
 strength, 207
 structural defects, 205f
 structure of atoms, 200ff
 thermal conductivity, 199
 work hardening, 207
 zone melting, 210f
Metallothermics, 209
Metallurgy, 208
 powder, 330
Metaphosphates, 92, 93
Metaphosphoric acids, 92, 93
Metasilicic acid, 182
Metavanadic acid, 324
Methane, 123, 133f, 137f
 series, 126
 spatial models of molecule, 124,
 125
 structure, 123f
Methanol, 150, 152
Methyl alcohol, 133f, 150, 152
Methyl amine, 166
Methyl cyclopropane, 131
Methyl ethyl ether, 154
Methyl ethyl ketone, 154
Methyl nitrate, 151
Methyl radical, 138
Mica(s), 182, 184
 white, 183
Microelements, 245
Microfertilizers, 245
Minium, 197
Misch metal, 313
Mispickel, 94
Mixtures,
 azeotropic, 31
 constant boiling, 31

- Molecule(s)**,
 dimer, 305
 electron-deficient, 280f, 301, 305
 segment model, 149
 spatial models, 130
 structure, 45ff, 53, 55, 128f
Molybdates, 331
Molybdenite, 330
Molybdenum, 325, 330f
 glance, 330
Molybdic acid, 331
Monazite, 310, 315
Monel metal, 369
Monocrystals, 205
Monodentates, 254
Monosaccharides, 161ff
Mortar, 286
- Naphthalene**, 145
Neodymium, 311
Neon, 339f, 342
Nephelite, 304
Neptunium, 314, 315
Niccolite, 368
Nichrome, 369
Nickel, 342f, 368ff
 alloys, 369
 arsenical, 368
 refining, 211
 silvers, 241
 sulphate, 370
 tetracarbonyl, 114, 211, 370
Nickel(II),
 hydroxide, 370
 oxide, 370
Nickel(III),
 hydroxide, 370
 oxide, 370
Nickeline, 369
Nimonic, 369
Niobium, 322, 324f
 carbide, 325
Nitrates, 85
Nitration, 84
Nitric acid, 82f
 concentration and reduction, 83f
 decomposition, 82
 production, 81, 85f
 salts, 85
Nitric oxide, 78
Nitrides, 69
Nitrites, 82
Nitrobenzene, 147
Nitrocellulose, 165f
Nitrocompounds, 147
Nitroethylene glycol, 153
- Nitrogen**, 66ff
 atmospheric, binding, 74ff
 cyanamide process, 74f
 cycle in nature, 86f
 dioxide, 80f
 fertilizers, 72f, 74
 hydrogen compounds, 68ff
 monoxide, 78ff
 electron configuration, 79
 energy-level diagram, 79
 occurrence, 67
 oxide, 78
 oxides, 77ff
 oxychloride, 84
 properties, 66, 68
 trichloride, 70
 trifluoride, 70
 triiodide, 70
 in vital processes, 73f
- Nitroglycerine**, 153
Nitron, 173
Nitronium, 81
Nitrophoska, 94
Nitrosyl chloride, 84
Nitrous acid, 80, 82
Nitrous oxide, 77
Nobelium, 314
Nucleic acids, 87f
- Number**,
 coordination, 252, 254
 and charge of central ion, 254
 octane, 140
 standard fineness, 246
- Nylon-6**, 176
Nylon-6,6, 176
- Oils**, 160f
 drying, 161
 gas, 139
 linseed, 161
 lubricating, 139, 189
 paraffin, 139
 solar, 139
- Olefins**, 141, *see also* Hydrocarbons, unsaturated
Oleic acid, 158
Oleum, 58
Orbitals, delocalized, 200
- Ores**,
 concentration, 209
 flotation, 209
 gravitational, 209
 magnetic, 209
 definition, 208
- Organic compounds**, 120ff, *see also* Hydrocarbons
 acyclic, 134

Organic compounds

- alicyclic, 135
- aliphatic, 134
- bonds, 122
- carbocyclic, 135
- classification, 134f
- with closed carbon atom chain, 135
- elementary analysis, 242
- heterocyclic, 135
- isomerism, 130ff
- nitrogen-containing, 136, 166ff
- with open carbon atom chain, 134
- oxygen-containing, 136
- saturated, 134
- sulphur-containing, 136
- unsaturated, 134

Organogens, 121**Organosilicons, 188f****Orlon, 173****Orthoboric acid, 303****Orthoclase, 183****Ortho-iodic acid, 39****Orthophosphates, 91****Orthophosphoric acid, 91****Orthosilicic acid, 182****Orthotelluric acid, 65****Osmium, 343, 371ff****octafluoride, 373****tetroxide, 372****Osmium(VIII),****fluoride, 373****oxide, 372****Oxalic acid, 121, 158****Oxyacids, 137****Oxygen, 40ff****difluoride, 33****isotopes, 42****oxidation number, 16,****preparation, 43f, 337****properties, 44****Oxyliquids, 45****Ozone, 45****detecting reaction, 47****structure of molecule, 45ff****Palladium, 343, 371f, 374f****Palladium(II) chloride, 375****Palmitic acid, 158****Paraffins, 137****Parchment paper, 165****Paris green, 243****Pearlite, 349, 357****Peat, 117, 118****coke, 117****Pentane, 131****Peracids, 61****Perbromates, 38f****Perbromic acid, 39****Perchlorates, 36****Perchloric acid, 36****Perchlorovinyl resin, 172****Perhydrol, 15****Periodates, 39****Periodic acid, 39****Perlon, 176****Permalloy, 369****Permanganates, 335f****Permanganic acid, 334f, 337****Permanganic anhydride, 337****Peroxides, 16****Perrhenates, 338****Perrhenic acid, 337, 388****Perrhenic anhydride, 338****Persulphates, 62****Persulphuric acid, 61f****hydrolysis, 15****structure, 61****Pesticides, 50, 58, 115, 243, 363****Petrolatum, 139****Petroleum(s), 139, 144****ether, 139****fractional distillation, 139****products, 139****Petrols, 139****Phase diagram(s),****alloys, 212ff****forming chemical compounds,****220f****with limited solubility, 219f****mechanical mixture, 214ff****with unlimited solubility, 217ff****application, 22****iron-carbon, 345ff, 356f****lead-antimony system, 214ff****lead-tin system, 218, 219f****magnesium-lead system, 220f****mechanical mixture alloys, 214ff****metal systems, 212ff****silver-gold system, 217ff****Phenol(s), 136, 150f, 153****dissociation constant, 151****Phenolates, 151****Phenoplasts, 175****Phenyl acetate, 159****Phenyl radical, 145****Phosgene, 114****Phosphates, 91****Phosphides, 89****Phosphine, 90****Phosphonium, 90****Phosphoric acids, 91f****Phosphorite, 87, 284****Phosphorous acid, 91****Phosphorus, 66, 87f****allotropic modifications, 88**

- Phosphorus,
 black, 89
 halides, 90
 oxides, 90f
 pentachloride, 90
 red, 88f
 trichloride, 90
 white, 88
Pitch blende, 315
Plaster of Paris, 57
Plastics, 170
 phenolic, 175
Platinic acid, 374
Platinum, 343, 371f, 373f
Platinum(II) chloride, 374
Platinum(IV) chloride, 374
Platynite, 369
Plumbates, 197
Plumbites, 196
Plutonium, 314, 315
Polonium, 40
Polyacrylates, 172f
Polyacrylonitrile, 172f
Polyamides, 169, 176
Polybutadiene, 174
Polycumulene, 103
Polydentates, 254
Polyenes, 141
Polyesters, 175f
Polyethylene, 171
 terephthalate, 176
Polyhalides, 259
Polymerization,
 degree, 171
 resins, 170f
Polymers, 169ff
 linear, 281
Polymethyl acrylate, 173
Polymethyl methacrylate, 173
Polynitrocompounds, 147
Polypeptides, 169
Polyphosphates, 92
Polyphosphoric acids, 92
Polypropylene, 171f
Polysaccharides, 164ff
Polystyrene, 172
Polysulphides, 52
Polytetrafluoroethylene, 172
Polythionates, 63
Polythionic acids, 63
Polyvinyl chloride, 172
Polyynes, 141
Potash, 112
 caustic, 237
Potassium, 230, 237f
 carbonate, 112
 chlorate, 35f
 chloride, 31
Potassium
 chromate, 327, 328
 cyanide, 116
 dichromate, 327, 329
 ferrate, 367
 hexacyanoferrate(II), 365f
 hexacyanoferrate(III), 366
 hydroxide, 237
 hydroxoplumbite, 195
 manganate, 335
 nitrate, 85
 perchlorate, 36
 permanganate, 335ff
 salts, 231
 silicate, 182
 sulphate, 57
 tetrafluoroberyllate, 281
Praseodymium, 311
Precipitate, 94
Pressure, dissociation, 285
Principle, circulation, 76
Process(es),
 Bessemer, 354
 carbonyl, 211
 chamber, 60
 contact, 59f
 converter, 354
 cyanamide, 74f
 hydrogenation, 14
 hydrometallurgical, 208
 iodide, 211
 open hearth, 354
 photographic, 248
 pyrometallurgical, 208
 saccharification, 164
 Solvay, 111
Promethium, 311
Propane, 125
Propanoic acid, 157
Propyl bromide, 131
Propyl radical, 138
Protactinium, 314
Proteins, 168f
Protium, 9
Prussian blue, 366
Prussiate of potash,
 red, 366
 yellow, 365f
Pyrite(s), 48, 343
 coal, 59
 flotation, 59
 iron, 48, 52, 53
Pyrocerams, 186
Pyrolusite, 334
Pyrolysis, 143
Pyrophosphates, 92
Pyrophosphoric acid, 92
Pyrosulphates, *see* Disulphates

- Pyrosulphuric acid, *see* Disulphuric acid
- Quartz, 181
- Radium, 277f
- Radon, 339f
- Rayon, viscose, 166
- Reaction(s),
 in blast furnaces, 353
 for carbonate, 109
 catalytic, 13, 15, 75, 114, 152, 156
 for chloride ions, 32
 combination, 142
 esterification, 159
 halogenation, 146
 hydrogen-oxygen, 13
 for iron(III) salts, 365
 Kucherov's, 156
 moisture detecting, 12
 nitration, 147
 oxidation-reduction, 197, 292f, 329
 direction, 97
 for ozone, 47
 polycondensation, 170
 polymerization, 143, 170, 171
 for potassium, 374
 reversible, 327f
 saponification, 160
 silver mirror, 155
 for sulphate ion, 57
 sulphonation, 146
 for unsaturated hydrocarbons, 143
 Zinin, 167
- Reagent(s),
 Schweizer's, 166
 for sulphate ion, 57
 for transition metal cations, 257
- Refrigerants, 31, 150
- Resins,
 condensation, 175
 perchlorovinyl, 172
 phenol formaldehyde, 175
 polymerization 170f
- Rhenium, 333, 337f
- Rhenium(VII) oxide, 338
- Rhodium, 343, 371f
- Ring, benzene, 135, 145
- Rock crystal, 181
- Rubber(s), 173
 butadiene-nitrile, 175
 butadiene-styrene, 174
 copolymer, 174f
 raw, 173
 synthetic, 174
 vulcanization, 50, 173f
- Rubidium, 230, 232f
- Ruby, 307
- Rule, Hund's, 265f
- Ruthenium, 343, 371f, 373
 tetroxide, 373
- Ruthenium(VIII) oxide, 373
- Rutile, 320
- Saccharose, 163
- Sal ammoniac, 73
- Salicylic acid, 159
- Salt(s),
 acid, 109f
 complex, 244f
 double, 58, 243
 mixed, 34
 normal, 109f
- Saltpetre, 85
 Chile, 85
- Samarium, 341
- Sand, 181
- Sapphire, 307
- Scandium, 310f
- Scheelite, 332
- Selenates, 64
- Selenic acid, 64
- Selenides, 64
- Selenium, 40, 63f
- Selenous acid, 64
- Semiconductors, 64, 178, 190f, 204
 electrical properties and temperature, 204
 energy bands, 203f
- Series,
 acetylene, 127, 141
 aromatic, 135, 144
 ethylene, 127, 141
 fatty, 134
 general formulas, 138, 114, 144
 homologous, 126, 138
 methane, 126
 saturated hydrocarbons, 126, 138
 monovalent radicals, 138
 physical properties and molecular mass, 139
 spectrochemical, 265ff
- Sextet, electron, aromatic, 148
- Siccatives, 161, *see also* Desiccants
- Siderite, 343
- Silanes, 179f
- Silica, 177, 181
- Silica gels, 182
- Silicates, 177, 182
 natural, 182
 formulas, 182f
- Silicic acids, 181f

- Silicides, 179
- Silicofluoric acid, 180
- Silicofluorides, 180
- Silicon, 101, 177f
 - carbide, 108, 179
 - chains, 125
 - dioxide, 177, 181
 - fluoride, 180
 - tetrachloride, 180
- Silumins, 307
- Silver, 238f, 245ff
 - amalgam, 296
 - bromide, 247, 248
 - chloride, 31f, 247, 248
 - complex compounds, 247f
 - fluoride, 247
 - glance, 245
 - iodide, 247
 - nitrate, 247
- Silver(I) oxide, 246f
- Similarity, diagonal, 280, 300
- Sitalls, 186
- Slags, 208
- Slaking, lime, 285
- Smaltite, 367
- Smithsonite, 111, 290
- Soaps, 158
- Soda, 111, 231
 - ash, 111f
 - baking, 111
 - bicarbonate, 111
 - caustic, 235
- Sodium, 230, 234ff
 - acetate, 157
 - amalgam, 234, 296
 - amide, 70
 - carbonate, 111
 - chloride, 31, 231
 - occurrence, 19f
 - cyanide, 116
 - dichromate, 329
 - diuranate, 316
 - ethylate, 151
 - fluosilicate, 180
 - hydrogen carbonate, 111
 - hydroxide, 235ff
 - hydroxoberyllate, 279
 - hydroxostannate, 193
 - hydroxozincate, 293
 - nitrate, 67, 85, 231
 - nitrite, 82
 - oxide, 234
 - peroxide, 235
 - phenolate, 151
 - plumbite, 196
 - silicate, 182, 184
 - sulphate, 57, 231
 - sulphide, hydrolysis, 52
- Sodium,
 - superoxide, 235
 - tetraborate, 303
 - tetrahydroxoaluminate, 306
 - thiosulphate, 62f
- Solders, 99, 191
- Solution,
 - azeotropic, 55
 - Fehling's, 155
 - solid, 212
- Sphalerite, 290
- Sphene, 320
- Stannane, 194
- Stannic acids, 193
- Stannites, 192
- Stannous acid, 192
- Starch, 164f
 - conversion into glucose, 152
- Stearic acid, 158
- Steel(s), 350, *see also* Alloys
 - acid-resistant, 326
 - alloy, 360f
 - symbols, 361
 - austenite, 360, 361
 - Bessemer, 354
 - cadmium plating, 295
 - carbon, 359f
 - case-hardening, 359
 - chromium, 325f
 - deoxidation, 355
 - hardening, 356
 - heat-resistant, 324, 326, 361
 - heat treatment, 356ff
 - chemical, 359
 - high-speed, 332, 361
 - high-temperature, 361
 - killed, 355
 - magnetic, 361
 - manganese, 334
 - molybdenum, 331
 - nitriding, 359
 - open, 355
 - pressure treatment, 356
 - production, 351f
 - rimming, 355
 - with special properties, 361
 - stainless, 228, 324, 326, 331, 361
 - structural, 360
 - tempering, 356
 - high, 359
 - low-temperature, 358
 - moderate-temperature, 358f
 - tool, 332, 360f
 - toughening, 359
 - tungsten, 332
- Stellites, 333, 367
- Stereoisomerism, 131, 132f, 262
 - mirror, 132

- Stereoisomers, 131
 Stibine, 98
 Stibnite, 98
 Strontianite, 288
 Strontium, 277f, 288f
 carbonate, 289
 hydroxide, 289
 oxide, 289
 salts, 289
 sulphate, 57, 289
 Styrene, 145
 Substances, *see also* Compound(s)
 inorganic, 120
 mineral, 120
 organic, *see also* Hydrocarbons, Or-
 ganic compounds.
 behaviour when heated, 122
 quantitative analysis, 122
 synthesis, 121
 Sugar,
 beet, 163
 cane, 163
 fruit, 163
 grape, 161, 162
 inverted, 163
 Sulphates, 57
 solubility products, 57
 Sulphides, 51f
 Sulphites, 54
 Sulphonic acids, 136, 146
 Sulphur, 40f, 47ff
 crystals, 48, 49
 dioxide, 53
 production, 59
 structure of molecule, 53
 flowers, 48, 50
 halides, 63
 liquid, 49
 molecules, 49
 monoclinic, 49
 plastic, 49
 rhombic, 49
 rod, 48
 trioxide, 54f
 structure of molecule, 55
 vapour, 49f
 Sulphuric acid, 55ff
 dissociation, 57
 oxidizing properties, 56
 production, 59f
 chamber process, 60
 contact process, 59f
 reaction with metals, 56f
 salts, 57
 structure of molecules, 55
 Sulphurous acid, 53f
 Superphosphate, 93
 double, 93
 Sylvinite, 238
 Sylvite, 20
 Table salt, *see* Sodium chloride
 Talcum, 283
 Tantalum, 322, 324f
 carbide, 325
 Tautomerism, 163
 Tautomers, 163
 Technetium, 333
 Teflon, 26, 172
 Telluric acid, 65
 Tellurides, 64
 Tellurium, 40, 63
 Tellurous acid, 64
 Tenorite, 242
 Terbium, 311
 Terephthalic acid, 158
 Terylene, 176
 Tetraborane, 302
 Tetraboric carbide, 108
 Tetracyanoplatinic (II) acid, 374
 Tetradentate, 255
 Tetrafluoroethylene, 150
 Tetrathionic acid, 63
 Thallium, 299, 309f
 Theory,
 Butlerov's, chemical structure, 123
 coordination, 252ff
 crystal field, 264ff
 ligand field, 264
 organic compound structure, 123ff
 Thermochromizing, 224
 Thioacids, 62
 Thioalcohols, 136
 Thioarsenic acid, 97
 Thioarsenous acid, 97
 Thioethers, 136
 Thiophenols, 136
 Thiosalts, 62
 Thiostannates, 194
 Thiostannic acid, 194
 Thiosulphates, 62
 Thiosulphuric acid, 62
 structure, 62
 Thorium, 314, 315
 Thulium, 312
 Tin, 101, 191f
 alloys, 191
 amalgam, 296
 bronzes, 241
 dioxide, 193
 disulphide, 194
 gray, 191
 plague, 191
 tetrachloride, 194
 white, 191

- Tin(II),
 chloride, 192f
 hydroxide, 192
 oxide, 192
 sulphide, 194
 Tin(IV),
 chloride, 194
 hydride, 194
 hydroxides, 193
 sulphide, 194
 Tinstone, 191
 Titanite, 320
 Titanium, 319f
 carbide, 321
 dioxide, 321
 refining, 211
 white, 321
 Titanomagnetites, 320
 Toluene, 144f
 Tombac, 241
 Topaz, 181, 182
Trans-isomer, 261f
 Trichloromethane, 150
 Trilon B, 256f
 Trimethyl amine, 166
 Trinitrotoluene, 147
 Tripoli, 181
 Trisilane, 180
 Tritium, 9
 Trotyl, 147
 Tungstates, 147
 Tungsten, 325, 332f
 carbide, 333
 Tungstic acid, 332
 Turnbull's blue, 366
 Type metal, 89
- Uranates, 316
 Uranic acid, 316
 Uranic anhydride, 316
 Uraninite, 315
 Uranium, 314, 315
 hexafluoride, 316
 isotopes, 315f
 trioxide, 316
 Uranyl, 316
 Urea, 112, 121
 Vanadates, 324
 Vanadic anhydride, 324
 Vanadium, 322f
 oxides, 324
 Vaseline, 139
 Verdigris, 243
 Vinegar, 157
 essence, 157
 Vinyl chloride, 150
- Viscose, 166
 Vitalism, 120
 Vitallium, 367
 Vitriol(s), 53
 blue, 58, 243
 green, 58, 363
 white, 293f
 Vulcanization, rubber, 50, 173f
- Water,
 baryta, 289
 chlorine, 21, 33
 desalination, 288
 formation from elementary substances, 13
 hard, 286
 hardness,
 carbonate, 286f
 elimination, 288
 natural, 286f
 non-carbonate, 286f
 permanent, 286
 temporary, 286
 total, 286f
 hydrogen sulphide, 50f
 preparation, 288
 soft, 286
 softening, 287f
 Wax, paraffin, 139
 Wires, electrical, aluminium and copper, 307
 Witherite, 288
 Wolframite, 332
 Wood, 117, 118
- Xenon, 339f, 342
 fluorides, 23, 341
 hydroxide, 341
 trioxide, 341
 Xenonic acid, 341
 Xylolite, 283
- Ytterbium, 312
 Yttrium, 310f
- Zinc, 289f
 blende, 48, 290
 chloride, 294

hydroxide, 293
oxide, 293, 294
sulphate, 293f
sulphide, 294
Zincates, 293
Zircalloys, 322

Zirconium, 210, 319, 312f
boride, 301
carbide, 322
dioxide, 322
Zone melting, 210f

TO THE READER

Mir Publishers would be grateful for your comments on the content, translation and design of this book. We would also be pleased to receive any other suggestions you may wish to make.

Our address is:

Mir Publishers

2 Pervy Rizhsky Pereulok

I-110, GSP, Moscow, 129820

USSR

Printed in the Union of Soviet Socialist Republics

Problems and Exercises in General Chemistry

N. GLINKA, D.Sc.

This is a training aid in general chemistry for students of higher educational institutions not majoring in the subject. It has been revised quite considerably (the previous twentieth Russian edition was published in 1973) in order to be used in conjunction with the latest twenty first edition of the author's *General Chemistry*. Each section has a brief theoretical introduction and examples showing how to solve typical problems. Many sections of the book contain questions contributing to full coverage of the material. All physicochemical quantities are expressed in SI units. The appendices contain all the reference data needed for solving the problems.

The book will be a useful aid for self-education in the fundamentals of chemistry and for students at chemical technical schools.

Physical Chemistry. Vol. I

Edited by Ya. GERASIMOV, Corr. Mem. USSR Acad. Sc.

This book is the first volume of a two-volume university course in physical chemistry, and deals with the fundamentals of chemical thermodynamics, thermodynamics of solutions, chemical and heterogeneous equilibria, and surface phenomena and adsorption. A special chapter is devoted to gas chromatography.

The book is intended for students of chemical faculties and universities, and will also be found useful by postgraduate students and teachers of physical chemistry. The authors presume that the book will be understood by readers who are studying physical chemistry for the first time and have a knowledge of mathematics and physics within the scope of the usual courses in these subjects adhered to by chemical faculties.

Physical Chemistry. Vol. II

Edited by Ya. GERASIMOV, Corr. Mem. USSR Acad. Sc.

This book is the second volume of a two-volume university course in physical chemistry, and deals with the kinetics of chemical reactions, chain reactions, reactions in electrical discharges, catalysis, electrochemistry, electromotive forces and chemical sources of current.

The size of the book is due mainly to the fact that the authors did everything possible to set out the fundamentals and their mutual relationship as understandable as possible. The mathematical deductions are given in sufficient detail, and in a simple manner.

The book is intended for students of chemical faculties of universities, and will also be found useful by postgraduate students and teachers of physical chemistry.

Selected SI Units

	Quantity	Unit	
		Name	Symbol
Basic Units	Length	metre	m
	Mass	kilogram	kg
	Time	second	s
	Electric current	ampere	A
	Temperature	kelvin	K
	Amount of substance	mole	mol
Derived Units	Force	newton	N ($\text{kg}\cdot\text{m}/\text{s}^2$)
	Pressure	pascal	Pa (N/m^2)
	Energy, work, amount of heat	joule	J ($\text{N}\cdot\text{m}$)
	Power	watt	W (J/s)
	Quantity of electricity	coulomb	C ($\text{A}\cdot\text{s}$)
	Electric voltage, electric potential	volt	V (W/A)
	Electrical resistance	ohm	Ω (V/A)
	Electrical conductance	siemens	S (A/V)

Conversion of Selected Non-System Units to SI Units

Quantity	Unit	Conversion factor to SI
Length	micrometre (μm)	$1 \times 10^{-6} \text{ m}$
	angstrom ($\text{\AA}$)	$1 \times 10^{-10} \text{ m}$
Pressure	atmosphere (atm)	$1.01325 \times 10^5 \text{ Pa}$
	millimetre of mercury (mmHg) or torr	133.322 Pa
	bar	$1 \times 10^5 \text{ Pa}$
	electron-volt (eV)	$1.60219 \times 10^{-19} \text{ J}$
Energy, work, amount of heat	calorie (cal)	4.1868 J
	kilocalorie (kcal)	4186.8 J

Fundamental Constants

Speed of light in free space	$c = 2.9979246 \times 10^8 \text{ m/s}$
Charge of an electron	$e = 1.602189 \times 10^{-19} \text{ C}$
Planck's constant	$h = 6.62618 \times 10^{-34} \text{ J}\cdot\text{s}$
Avogadro's constant	$N_A = 6.022045 \times 10^{23} \text{ mol}^{-1}$
Faraday's constant	$F = 9.64846 \times 10^4 \text{ C/mol}$
Molar gas constant	$R = 8.3144 \text{ J/(mol}\cdot\text{K)}$

23 P.75

MIR PUBLISHERS of Moscow publishes Soviet scientific and technical literature in twenty five languages including all those most widely used. Titles include textbooks for higher technical and vocational schools, literature on the natural sciences and medicine (including textbooks for medical schools), popular science and science fiction. MIR's authors are leading Soviet scientists and engineers from all fields of science and technology, among them more than forty Members and Corresponding Members of the USSR Academy of Sciences. Skilled translators provide a high standard of translation from the original Russian. Many of the titles already issued by MIR PUBLISHERS have been adopted as textbooks and manuals at educational establishments in France, Switzerland, Cuba, Syria, India, Brazil and many other countries.

MIR PUBLISHERS' books in foreign languages can be purchased or ordered through booksellers in your country dealing with V/O Mezhdunarodnaya Kniga, the authorised exporters.

About the book

Professor N. Glinka's textbook systematizes the theoretical aspects and includes an extensive collection of reference data for the course in general chemistry. Great attention is given to the structure of atoms and molecules, the laws of chemical reactions, and oxidation-reduction, processes. The book has been very popular in the Soviet Union and other countries for many years. During the author's life, it saw 12 editions in Russian and was repeatedly published in other languages. The time that has elapsed after the author's death, however required the introduction of appreciable amendments into the book, first of all because of the deep penetration of chemistry into many branches of the national economy and of the tremendous growth in the volume of the factual material of chemistry. The required revision of the textbook was carried out in its sixteenth Russian edition (1973).

An additional revision of the book mainly due to the transition to SI units of physical quantities and the associated alterations in the terminology was carried out in the nineteenth Russian edition (1977). The present English text has been translated from the 21st Russian edition (1980), and to facilitate work with the book, has been divided into two volumes. The book is intended for students of higher educational institutions not majoring in chemistry. It will also be very helpful for persons studying the fundamentals of chemistry independently, and for students of chemical technical schools and the senior classes of secondary schools.

