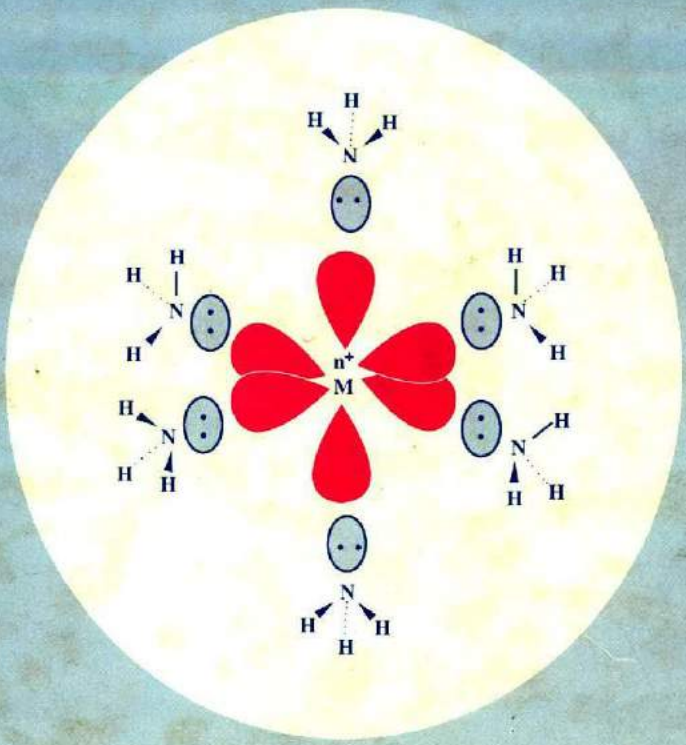
INTRODUCTION TO

MODERN INORGANIC CHEMISTRY



S. Z. HAIDER

Compiled by

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INTRODUCTION TO

MODERN INORGANIC CHEMISTRY

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To

All those devoted and inspiring teachers who are striving to spread the light of knowledge and imprint the qualities of head and heart into the minds of our younger generations for enlightenment and the upliftment of the destiny of Bangladesh in the new Millennium.

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PREFACE TO THE SECOND EDITION

The contents of the second edition have been slightly changed and the printing errors present in the first edition of the book have been eliminated. Some changes in the nomenclature and symbols of the new elements have been incorporated. The organisations of the descriptive chemistry have been modelled and interlaced with conceptual approach on structural principles. The book is primarily intended to meet the demands of the students studying for science graduations, engineering and medical sapplementary professional conceptual courses of the colleges and universities of Bangladesh.

Suggetions for further improvements of the texts from the teachers and students are cordially invited.

PREFACE TO THE FIRST EDITION

This book has been published as a result of the pressing demands both of the students and the teachers for a modern text book in inorganic chemistry in a style which is comprehensible to the concerned community according to the local requirements of studies and of examinations. The book deals with the basic concepts in inorganic chemistry normally required for students of degree courses but also covers to a great extent the introductory materials for the honours and post graduate courses of the universities of Bangladesh. However, the students are advised to supplement their studies for extended knowledge from foreign advanced books and journals.

In the present text the descriptive materials have been reduced to the minimum and emphasis has been given to conceptual approach of inorganic chemistry so as to create critical thinking and the development of the spirit of enquiry in the minds of the students. These factors are essential for the acquisition of higher studies and specialized knowledge for useful practical applications of chemical principles.

The structures of matter at the molecular level which is the basis of the study of chemistry has been introduced as a logical sequence of events leading to the contemporary view points in respect of structural chemistry involving minimum but precise use of mathematics. A concise description of the survey of the elements according to the Periodic Table based primarily on electronic configurations of elements and some of their important compounds has been included to indicate the practical significance and importance of the study of inorganic chemistry. The book shall be helpful for an introductory conceptual and practical courses for both the students of medicine and engineering.

I take the opportunity to mention that I have derived great help from a large number of text books, reference books and journals published in the U. S. A., the U. K. and other countries. I particularly mention the various issues of the Journal of Chemical Education and Education in Chemistry.

I am grateful to my colleagues and teachers of various educational institutions for their encouragement to get this book published in a new modified form to cover introductory syllabuses for degree, honours and post-graduate courses in easy English generally followed by the students of science.

It is a great pleasure to acknowledge the efforts of Mr. S. M. Haider of Friends International, for undertaking the responsibility of publishing the book. I also express my thanks to Mr. A. K. M. Abdul Hai of Asiatic Press, Dhaka for arranging the printing of the book. Thanks are due to M. Yousuf Ali Khan for taking all the troubles of computer compose for the text. and some of the figures. Thanks are also due to my wife Syeda Saleha Khatoon who helped me in organising the materials and admirably endured the vexations in course of writing of this book.

It is next to impossible to produce a completely error-free book locally and some errors might have crept in the form of printers devil. I express my gratitude to Late Dr. Syed Jamal Quader, formerly Head of the Analytical Research Division, BCSIR, Dhaka for making painfully a list of errors of the original text. The corrections have been incorporated in the present book. The author shall be obliged to all those who would kindly communicate the information about the errors of printing or of statement of facts and figures to help rectify the same in future editions.

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April 1994

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CHAPTER-1

THE STRUCTURE OF ATOM

The physical and the chemical properties of elements and their compounds are essentially correlated with the structure of atoms. A systematic knowledge of the structure of atoms is, therefore, necessary for the study of modern inorganic chemistry. In fact, the knowledge of structure of atoms has made it possible for the subject of chemistry to be systematized in such a way that it is easier to understand and remember. The chemical reactions and the forces between atoms in molecules can be explained in terms of the structure of atoms. It will be noted that structure and properties of matters are essentially functions of electronic configurations of the atoms of elements.

The Atomic Theory

It may be mentioned that the idea that matter is constructed of ultimately indivisible particles is as old as science itself. The Greek philosopher, Democritus, is attributed to have originated the atomic concept of matter as opposed to the view of Aristotle that matter is continuous and that there is no limit of its subdivision. The latter view has been completely discarded and in 1803 John Dalton with the help of experiments placed the atomic hypothesis on a useful scientific basis and developed the concept of atomic weights which became the basis for the laws of chemical combinations. The quantitative concepts of atoms subsequently led to a considerable advancement of the science of chemistry both in the theoretical and practical fields. Among the experimental results and relationships supporting the atomic theory mention may be made of Gay-Lussac's law of combination of gases by volume, the law of multiple proportion of Dalton, Faraday's laws of electrolysis and Avogadro's hypothesis

pointing to the existence of molecules and well as atoms. Avogadro's Law provided a basis for the determination of molecular weights. It is the regular arrangement of atoms which gives many solids their crystalline shapes.

Avogadro Number

It may be pointed out that the actual number of molecules in a gram molecule or the number of atoms in a gram atom of any substance has been determined accurately in many different ways which are entirely independent of each other. This number, denoted by N, has a value 6.02×10^{23} molecules per mole (or atoms per gram atom) and is called Avogadro Number. It is a fundamental constant in science with many important applications. The best value for N, 6.023×10^{23}, has been obtained by averaging values from a number of different types of accurate measurements. With the help of Avogadro Number, the weight of a single atom or a molecule can be obtained by dividing the respective atomic or molecular weight by N. For instance, the weight of one single atom of hydrogen is $1.008/6.02 \times 10^{23} = 1.67 \times 10^{-24}$ gram; and the weight of a molecule of carbondioxide is equal to the molecular weight of CO_2 divided by N, i. e. $44.01/6.02 \times 10^{23} = 7.30 \times 10^{-23}$ gram.

A passing reference may be made regarding a notable modification of the atomic theory by Prout in 1815. According to Prout's hypothesis matter was made up of multiples of a fundamental substance which he suggested might be hydrogen. The idea of an ultimate particle in the form of hydrogen atom, of which all other atoms are made, has long been discarded and discredited by accurate determinations of atomic weights, but the idea certainly inspired the scientists for further speculations as regards the composition of matter.

Atoms as Carriers of Electricity

Atoms act as carriers of electricity when an electric current is passed through a salt solution. Faraday discovered that the equivalent weights of different substances were liberated at the electrodes by the passage of the same quantity of electricity. It can be concluded that Faraday's Laws of electrolysis would not have been valid until and unless matter (electrolytes in solution) would have been

made up of electrically charged atoms or ions capable of free movement in solution between two electrodes by the passage of electricity. Accurate determinations have shown that the liberation of 1 gram equivalent of any substance requires the passage of 96,493 absolute coulombs of electricity, and this quantity, represented by F, is known as a *Faraday*. Thus the quantity of electricity which will deposit one g. atom of a monovalent element is called the "*Faraday*". (A coulomb is the quantity of electric charge passing a point in an electrical circuit in one second with one ampere current.)

An obvious deduction from Faraday's laws is that 1 g. equivalent of any ion carries the same amount of electric charge, i. e., F coulombs. Since 1 g. atom contains N number of atoms, it can be deduced that N atoms of a univalent substance carry F coulombs. Similarly, N number of atoms of a bivalent, trivalent and n-valent substances will carry 2F, 3F and nF coulombs respectively. Hence it can be generalized that 1 single atom of an element is associated with nF/N coulombs of electricity where n is the charge of the ion. Again, since n is an integer, it follows that the charge of electricity carried by any single ion is a multiple of the fundamental quantity or smallest unit represented by F/N. This is the unit of electric charge for which Stoney in 1891 proposed the name *electron*. It was not clear whether these units of electricity carried by atoms are positive or negative or whether electrons of both signs exist and form compounds with the originally neutral atoms. The value of $\frac{F}{N} = \frac{96{\cdot}500}{6.023 \times 10^{23}}$ coulombs $= 1.60 \times 10^{-19}$ coulombs $= 1.60 \times 10^{-20}$ emu (electromagnetic unit), or $= 4.8024 \times 10^{-10}$ esu (electrostatic unit). Hence the charge $e = \frac{F}{N}$ is the smallest charge of an ion. Thus the charge of an ion of Na^+ is e, that of bivalent Mg^{+2} is $2e$, and that of trivalent Al^{+3} is $3e$.

Passage of Electricity Through Gases

Electricity does not pass under normal condition between electrodes. Even if it does, it does in the form of a sudden spark in the presence of air or gases under very high voltage.

But when the gas is enclosed in a glass tube and pressure inside the tube is reduced, the conductivity of the rarefied gases is greatly increased and electricity begins to pass giving luminous and dark spaces at first; when the pressure is

reduced to about 0.01 to 0.001 mm., rays are sent out in straight lines from the cathode, which become evident when these rays strike the sides of the glass tube to produce green fluorescence (Fig. 1—1). These rays are known as cathode rays

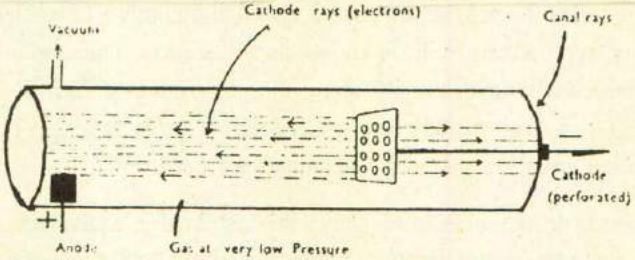


Fig. 1—1. Production of cathode rays and canal rays (positive ions) in a discharge tube.

and are deflected in electric and magnetic fields indicating that these carry electric charge which was proved to be of negative sign by J. J. Thomson.

The deflection of the cathode rays towards the positive pole of the electric field conclusively proves that the rays are associated with negative charges (Fig. 1—2).

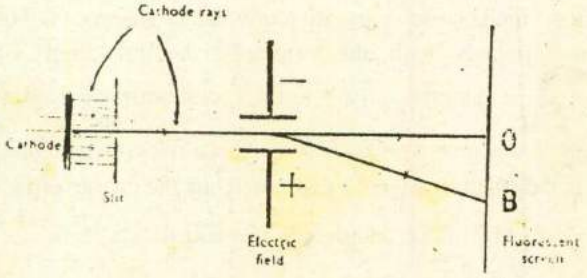


Fig. 1–2 Electrons attracted towards the positive pole of the electric field.

A thin beam of cathode rays strikes at point O on the screen when the electric field in not applied, as shown diagrammatically in Fig. 1-2. When the electric field is applied, the point O moves to B showing that the beam has been attracted towards the positive pole of the electric field.

Determination of e/m: The cathode rays are passed through a small slit (Fig. 1-2) and the narrow beam taken in-between the plates of electric field is

allowed to be focussed on the fluorescent ZnS screen. When the electric field is applied under high vacuum the movement of the bright spot at point O to point B is connected with the charge-to mass ratio of the cathode particle. Similarly, if the cathode beam is subjected to the influence of magnetic field instead of the electric field, the bright spot on the screen describes a circular path. Both the electric and magnetic field are applied simultaneously and the forces are so adjusted that fluorescent spot does not move from its original position at point O. Under this condition the force due to electric field on the cathode particles becomes equal to the force due to the magnetic field.

If e be the charge and m be the mass of a cathode particle moving with velocity v, and I and H be the respective intensities of the electric and magnetic fields then under the conditions of no deflection, we get,

Force due to magnetic fields $H.e.v$ = force due to electric field, $I.e$; that is,

$$H.e.v = I.e \text{ or } v = I/H$$

Thus the velocity of the cathode particles can be found. Now, on subjecting the cathode beam to the action of magnetic field alone and noting the radius r of the circular path, it is observed that the centrifugal force $\frac{mv^2}{r}$ is equal but opposite to the force due to applied magnetics field; that is $H.e.v = \frac{mv^2}{r}$) or

$$\frac{e}{m} = \frac{v}{rH}$$

Since $v = I/H$, the ratio e/m can be obtained from the equation:

$$\frac{e}{m} = \frac{I}{rH^2}$$

Thus it was proved that cathode rays consist of particles carrying negative charges and ultimately given the name electron, since they are apparently identical with the unit of electricity associated with the ions in solution suggested by G. J. Stoney. The electrons produced in the cathode rays are in the free state. The properties of the cathode rays were always the same, no matter what gas was used in the tube or what electrode materials were employed. Electrons are also emitted by certain metals when heated to high temperatures. The process is called thermal emission of electrons. Electrically heated metal filaments in vacuum tubes produce electrons which are employed in radio and television. Electrons are also emitted from active metals such as sodium on exposure to light. X-rays also liberate electrons from all types of matter. These photoelectric electrons are employed in photoelectric cells. Radio-elements emit β-rays which are also electrons moving with great speed.

Thus all electrons are identical, irrespective of their source or method of production, and although their velocities vary, their other properties, especially the "charge to mass" ratio *e/m* remained constant. But a knowledge of *e/m* did not give the knowledge of the values of *e* or *m* of an electron.

Determination of charge e : A number of methods have been developed for determination of charge on an electrical particle, The three important methods are-(i) Wilson's cloud chamber method, (ii) Millikan's oil drop method and (iii) Compton's X-ray diffraction method.

Wilson used two horizontal brass plates in a cloud chamber to study the behaviour of a charged fog in the presence of an electric field. The two plates were kept at distances from 4 to 10 cm apart. On applying electric potential to the parallel plates it was noticed that the fog fell at a different speed than under the normal influence of gravity. The ratio of the two velocities enabled to calculate the electronic charge. But the value of "*e*" so determined was not very accurate.

Millikan's Oil Drop Method : Small drops of oil can be charged electrically by subjecting them to radiations with X-rays or ultraviolet rays or by radio-elements. Millikan used an apparatus shown schematically in Fig. 1-3 in which electrically charged oil drops were sprayed by means of an atomizer. The upper metal plate has a number of small holes through which a few droplets enter the region between the charged plates. A droplet of oil tends to fall downward due to gravitational force. However, if the top plate is given the charge opposite to that of the drop, the drop is attracted upwards, By adjusting the strength of electric field the droplet may be made to remain suspended and stationary between the two charged plates. This happens when the upward

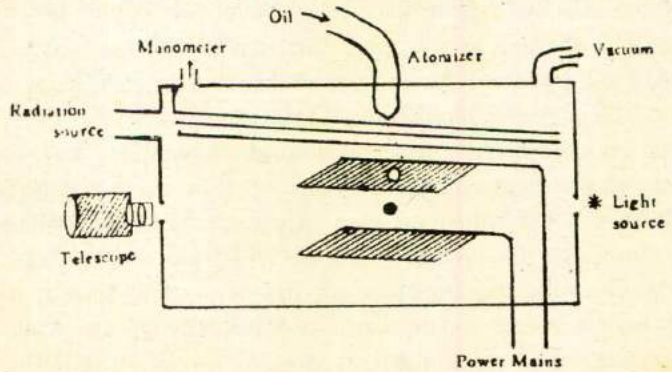


Fig. 1–3. Schematic sketch of Millikan's apparatus for the determination of *e*.

electrostatic force becomes equal to the downward gravitational force. This situation is observed between the cross-wires of the telescope while the region between the two plates is illuminated by a source of light.

In a series of experiments Millikan determined the mass of the oil drops (m_o) by measuring the radii (r_o) of the drops and the density of the oil (d_o) by using the relationship

$$m_o = \frac{4}{3} \pi r_o^3 d_o$$

The radii (r_o) of the drops were calculated by observing the velocity of fall (v_1) of the drops under gravity by noting the time taken by the drop to travel between the two sets of cross-wires of the telescope and using the relationship

$$v_1 = \frac{2}{9} \frac{g r_o^2 (d_o - d_a)}{\eta}$$

where g is the acceleration due to gravity, d_o and d_a are the densities of the oil and air respectively and η is the viscosity of air. Under the conditions when downward gravitational force is equal to the upward electrostatic force (charged oil drop remains stationary between the plates) we have

$$I.\, e_o = m_o.\, g \quad \text{or} \quad e_o = \frac{m_o g}{I}$$

where I is intensity of the electric field, e_o is the charge on the oil drop which can be easily computed.

If the upward electrostatic force, $I.\, e_o$, is greater than the downward gravitational force, $m_o g$ ($I.\, e_o > m_o g$), then the velocity v_2 of the oil drop for upward journey can be measured by timing the distance of rise between the cross-wires of telescope. Under this condition we have

$$\frac{v_2}{v_1} = \frac{I.\, e_o - m_o g}{m_o g}$$

$$\text{Therefore } e_o = \frac{m_o g}{I.v_1} (v_1 + v_2)$$

The charge e_o on the oil drops varied from drop to drop in successive experiments but Millikan observed that the values always indicated to be an

integral multiple of a single unit. Millikan concluded that electrical charge is quantized and that any electrical charge must be a some integral multiple of a fundamental unit of charge. The smallest charge or the fundamental unit after modification was found to be equal to 1.602×10^{-19} coulombs per electron or 1.602×10^{-20} electromagnetic unit (emu) or equal to 4.803×10^{-10} electrostatic unit (esu), almost the same value as found from F/N. The mass of an electron was calculated to be equal to $\frac{1}{1839}$th part of the mass of one atom of hydrogen approximately.

From the above discussion it can be seen that the electron is a universal constituent of all matters and that it is much smaller in mass as compared with that of a single atom of hydrogen which is the lightest of all atoms. The comparative figures given below indicate the magnitudes.

Charge of an electron e	$= 1.602 \times 10^{-20}$ emu
	$= 4.803 \times 10^{-10}$ esu
1 emu	= 10 coulombs
Mass of one atom of hydrogen	$= 1.67 \times 10^{-24}$ g.
Mass of one electron	$= 9.11 \times 10^{-28}$ g.
$\frac{e}{m_H}$ in the case of hydrogen	$= 9.579 \times 10^{3}$ emu/g.
	$= 9.579 \times 10^{4}$ coulombs/g.
	$= 2.876 \times 10^{14}$ esu/g.
$\frac{e}{m}$ in the case of electron	$= 1.759 \times 10^{7}$ emu/g.
	1.759×10^{8} coulombs/g.
	5.274×10^{17} esu/g.

At this stage a rough idea can be had as to what happens when electric discharge takes place through rarefied gases. Why the conductivity of electricity is increased in high vacua? Under the impact of high voltage, a small portion of the gas in the tube is ionized which means it loses electrons easily. The free electrons are sufficiently accelerated to knock out electrons from other atoms and

molecules by sudden impact. Ultimately a large number of electrons are formed by collision with the gaseous molecules and since the pressure inside the tube is decreased considerably, the "free path" of molecules and ions becomes greater and the charged particles give rise to increased electrical conductivity. A state is finally reached at which a large number of electrons are continually being formed and are accelerated to very high velocities by the repulsive force of the cathode. Thus the cathode rays which constitute the electrons appear to move away form the cathode towards the anode.

It might also be realized that a stream of positively charged particles must also be moving in the opposite direction. Since atoms are electrically neutral and if the negative particles of the atoms are dislodged from it, evidently the positive part would also be produced during the process. Goldstein in 1886 discovered the positively charged ions in the cathode rays tube by a special device, i. e., by using a perforated cathode. The positively charged rays moving away from the anode passed through these perforations or canals and hence are known as *Canal Rays* (Fig. 1-1). The particles constituting the canal rays are found to be heavier than electrons and move very slowly. Determination of the charge to mass ratio in the case of canal rays or positive rays showed that it is not a constant quantity in this case and varied from gas to gas in the vacuum tube. The charges on the positive particles, unlike those on electrons, were found to vary in magnitude. Measurements indicated that each particle carried either a unit positive charge or a simple multiple of this unit. The unit positive charge was equal to the charge on the electron but of opposite sign. The mass of the positive particles was found to be minimum when hydrogen was used in the discharge tube than when any other gas was employed. The neutral atom can be made to form positive ions by the loss of one or more electrons. From this fact it can be concluded that an atom must contain one or more positive units. The simplest atom is obviously that of hydrogen and when it loses its electron the positive hydrogen ion (H^+) is known as *proton*.

After the discovery of electron in all types of atom, a vague idea was put forward regarding the structure of atom by Thomson. According to Thomson, an atom consists of a number of electrons distributed in a sphere of uniform positive electricity. The idea of nucleus in an atom was quite unknown.

Radioactivity and Atomic Structure

A further advancement in the idea of the structure of atom was provided by the discovery of radioactivity. The term radioactivity applies to the spontaneous disintegeration of atoms of certain elements, such as radium and uranium, into simpler elements with the simultaneous production of one or more of the three kinds of radiations emitted during the process. These types of rays are known as alpha (α) rys, beta (β) rays and gamma (γ) rays, These can be characterised by placing the radioactive material in a hole bored in a block of lead, and allowing the emitted rays to pass through strong electric or magnetic field as shown in Fig. 1—4.

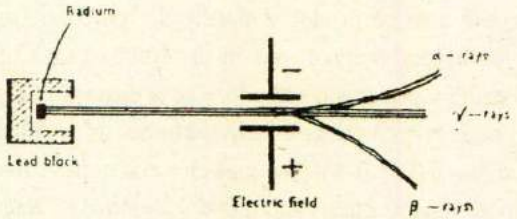


Fig. 1—4. α, β and γ-rays from radium.

The α-rays are deflected towards the negative pole of the electric field and consist of positively charged particles subsequently found to be doubly charged helium ion (He^{+2}). The β-rays are attracted towards the positive pole of the electric field and are, actually electrons moving with tremendous velocity approaching that of light (186,000 miles per second). The γ-rays are not affected by the electric field but are more penetrating having very short wavelengths similar to x-rays and affect photographic plate or film.

Scattering of β-rays by Metal Foils

Since β-rays are electrons moving with great velocities, it was thought that these may force their ways inside an atom and its effect may reveal something about its structure. For this purpose, a narrow parallel beam of β-rays from a radioactive source was directed on thin metal sheets, such as those of aluminium, silver, gold etc. It was noticed that the emergent beam was scattered and

divergence could be due to the repulsion of β-rays by the electrons present in the atoms of the metals (Fig. 1—5).

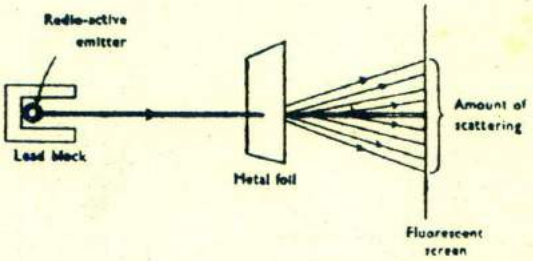


Fig. 1—5. Scattering of β-rays by metal foils.

Form the amount of divergence it was possible to calculate the number of electrons present in the metal atom and this was found to be approximately half of the atomic weight of the metal. Since each electron weighs only $\frac{1}{1837}$th part of one atom of hydrogen, it can be easily seen that the major part of the mass of an atom is associated with the positive electricity.

Scattering of α-rays and the Idea of Nucleus

α-particles are emitted from radioactive elements with great velocities, on the average about 180,000 miles per second. Rutherford in 1911 projected a beam of α-particles from a radioactive source upon a very thin gold foil. He found that most of the particles passed through the solid gold foil without deflection, and that only a few of them occasionally suffered abrupt back deflection as if the α-particles have met with some obstacles in their onward journey. From this experiment Rutherford assumed that the mass of an atom is concentrated in a central body called the Nucleus which is exceedingly small as compared to the total size of the atom. The electrons can be easily knocked out from the atoms and therefore constitute the external structure of the atom. The nucleus also carry the entire positive charge of the atom. When α-particles come in contact with such a system, there is little or no deflection of α-particles by the tiny electrons because of the mass and size of the particles. But α-particles can only turn back by hitting the nucleus not only because of their

obstacle but also due to repulsion by the positive charges on the nucleus as encounter with a massive shown in Fig. 1—6.

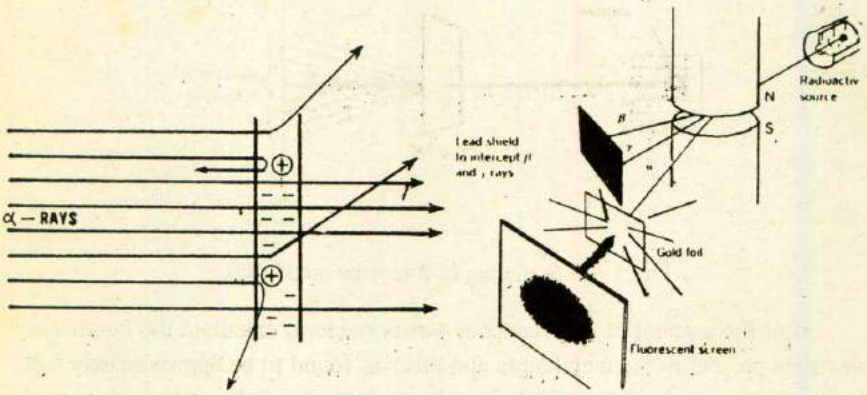


Fig. 1—6. Deflection of α-particles by nuclei in a metal foil.

Rutherford measured the nuclear charges of a large number of atoms and proved that the number of positive charges on the nucleus is, in many cases, approximately one-half the atomic weight of the element and also equal to the number of free electrons in the atom, since its charge is equal to that of all the free electrons.

If there were several nuclei in the atom, the ratio of specific heats at constant pressure Cp, and at constant volume Cv, i. e., Cp/Cv, could not be as high as 1.67 even for monoatomic gases.

Rutherford's Atom Model

Rutherford's solar system atom model may be described as follows :-

(1) An atom consists of a small nucleus containing all the positive charges of the atom and practically the whole of its mass.

(2) The nucleus is surrounded by a number of electrons equal to the number of positive charges on the nucleus.

(3) The electrons are in constant motion round the nucleus like that of planets round the sun in such a way that the electrostatic force of attraction between the electrons and positive nucleus is counterbalanced by the centrifugal force.

As mentioned before, the unit of positive charge in an atom is considered to be due to proton. Here it can be assumed that a nucleus consists of protons which provide all the positive charges and probably almost all the mass of the atom. But this idea is not correct. Since an atom is electrically neutral, it must consist of equal number of positive and negative charges. The problem of atomic weights remained to be solved.

Atomic Number

In 1914, Moseley worked out a method for determining the number of positive charges on the nucleus of an atom. The method used involved the measurement of the wavelengths of x-rays given off by various elements when employed as target. When the metal target is placed in the path of the high velocity cathode rays (electrons), electromagnetic radiations of short wavelengths are produced. These rays are very penetrating and are called x-rays. In order to study the x-rays produced when different elements or their compounds were used as targets, salt crystals such as those of potassium ferrocyanide were used as diffraction gratings to spread the x-rays into a spectrum similar to that when a beam of sunlight is passed through a glass prism.

When the spectra of x-rays produced in this manner are recorded on a photographic film, the lines in the photograph are characteristic of the material of which the target is made. Moseley arranged the x-ray spectra of different elements in the order of increasing atomic weights, and found that the heavier the elements the shorter the wavelengths of the principal lines in the spectra. The wavelength of any element differed from that of the next higher element by the same amount (Fig. 1–7). Thus there is, in an atom, a fundamental quantity which increases by regular steps as we pass from one atom to the next. This quantity can be the charge on the nucleus thus indicating a constant difference of

one proton in the nuclei of the atoms of adjacent elements in the Periodic Table. Thus all the elements can be arranged in the increasing order of the positive

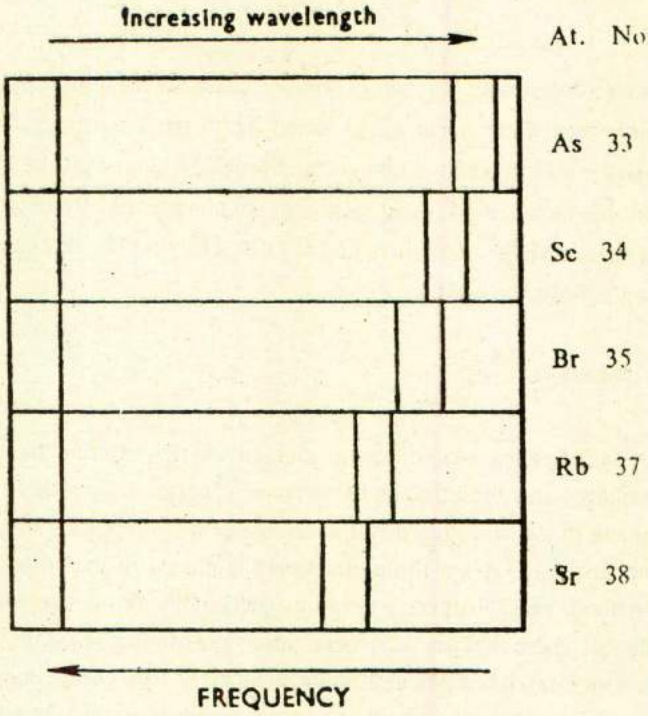


Fig. 1–7. X-ray spectra of Moseley. Note the greater shift in wavelength between Br (35) and Rb (37).

charge on the nuclei of their atoms instead of the atomic weights beginning with hydrogen. Thus the atomic number of an element can be defined as the number of positive charges on the nucleus of its atom. In effect, the atomic number is the number of protons in the nucleus. The number of electrons outside the nucleus in a neutral atom also gives its atomic number.

Fundamental Particles of Atom

An atom is the smallest particle of an element having its own chemical identity and properties. But the experiments described before indicate that atoms can be subdivided into smaller subatomic particles known as fundamental

particles. Quite a large number of particles have been identified from the subdivision of atoms. Most of the particles are quite unstable and their nature are not clearly known. For the purpose of the study of chemistry the three most important particles, namely *electron*, *proton* and *neutron*, are regarded as fundamental particles.

Electron : An electron is the smallest of the subatomic particles. As mentioned before, it has the unit electrical charge with negative sign Its mass is about $\frac{1}{1840}$ times less than that of a hydrogen atom or proton. The study of cathode rays provide a great deal of informations regarding the characteristics of electrons. Cathode rays have been proved to be streams of negatively charged electrons moving in an electric field with tremendous speed. These are deflected towards the positive pole of an electric field and also deflected at right angles to the applied magnetic field. The charge to mass ratio, *e/m* of an electron has been experimentally determined and found to be constant irrespective of the source and the method of production. Electrons appear to constitute the outer structures of atoms, since they are easily dislodged under the influence of electric field. Electrons are emitted from the surface of a substance exposed to the action of x-rays, ultraviolet rays and even on exposure to ordinary light. Electron beams are also produced from electrically heated metal filaments in vacuum tubes. β-rays from radioactive elements are also fast-moving electrons.

The chemical properties of elements and their compounds are mostly dependent upon the arrangement of the electrons in their atoms.

Proton : When an electron is lost from the lightest of all atoms, i. e., hydrogen, a positively charged particle is left. This particle is called a proton. It bears a unit positive charge (i. e., 1.602×10^{-20} emu) but is about 1839 times heavier than an electron. If the gas in the discharge tube is hydrogen, the positive rays formed after the discharge of electrons may consist of protons. The determinations of the charge to mass ratio, *e/m*, when hydrogen is used in the discharge tube, give the largest value for the positive ions. It is, therefore, assumed that positive ions from this source are the fundamental particles to which the name proton has been given. The value of *e/m* decreases with the increase in the mass of the particle and this depends upon the gas present in the discharge tube.

Neutron : Rutherford predicted the presence of neutral particles within the nucleus of an atom in order to account for the total mass of the atoms. Since an atom is electrically neutral, it must contain equal number of electrons and protons. But the atomic mass is much greater than the total masses of electrons and protons present in the atom. In 1932, Chadwick discovered neutron as a fundamental unit of atomic structure, He observed that when α-particles are used to bombard thin sheets of beryllium metal, uncharged particles are emitted. These neutral particles are called neutrons. They have a mass equal to 1.0087 on the atomic weight scale (i. e., approximately unity). It was later discovered that under certain conditions a neutron may disintegrate and form a proton and an electron. This may be the origin of the electrons composing the β-rays which are emitted by radioactive elements.

Composition of the Nucleus

The nuclei of atoms contain, for all practical purposes, both protons and neutrons except in the case of hydrogen atom which consists of a single proton. Each neutron and each proton has a mass of approximately 1 (on the basis of atomic weight of carbon, C = 12 *atomic mass unit* (*amu*). The atomic weight of an element is approximately equal to the sum of the weights of the total number of protons and the total number of neutrons in the nucleus (neglecting the small weight of the electrons present). The assignment of mass 12 to the isotope of C is defined as the new atomic mass scale by the International Union of Pure and Applied Chemistry (IUPAC) in 1962. Oxygen, O = 16.000, has previously been used as the standard *amu*. But at present the masses of all nucleus are expressed as a ratio of their masses to the mass of C^{12} = 12.000.

The protons and neutrons in the nucleus are held together by a force known as nuclear force. The picture of the nucleus is actually much more complex since a very large number of fundamental particles are supposed to be created by the interaction of the neutrons and protons. According to Heisenberg, a neutron in the nucleus sometimes is transformed into an electron and a proton. The electron might escape in the form of β-rays. This is known as *beta decay*. The change in mass for a beta decay is zero.

Mesons : In 1935, Yukawa suggested that when a proton and a neutron interact, a fundamental particle known as meson is absorbed by the neutron. There are two types of mesons having mass between 200 and 300 times that of an electron. The two types of mesons are π mesons and μ mesons. The π mesons at present are known ans *pions* and the μ mesons as *muons*. These may be positive, negative and neutral. In the exchange of positive pion the proton becomes a neutron and the neutron becomes a proton. In the same way a neutron may interact with a proton by emiting a negative pion. These interactions are represented as :

$$p \rightleftharpoons \pi^+ + n$$

$$n \rightleftharpoons \pi^- + p$$

It may be seen in the chapter on Nuclear Chemistry that the emission of an electron or a β-ray from a radioactive nucleus is evidently due to the transformation of a neutron into a proton and electron :

$$n \longrightarrow p + e$$

This transformation is known as *beta decay*. In this beta decay, the energy of the neutron should be equal to the energy of the products. But it has been found that both energy and momentum of the particles are changed. In order to preserve the conservation of energy and momentum in beta decay, Pauli suggested that the proton is retained in the nucleus and the electron and another particle called *neutrino* are emitted. Thus :

$$\text{Neutron} \longrightarrow \text{proton} + \text{electron} + \text{neutrino}$$

Existence of the free neutrino has since been established experimentally in 1956. Neutrino has charge zero and its mass is either zero or near about zero.

The present-day knowledge of the structure of the nucleus has progressed so far as to present a very complex situation. The multiplicity of fundamental particles has become a subject matter of a vast theoretical and experimental research embodied in the fields of nuclear physics and nuclear chemistry and is beyond the scope of this elementary text book. However, the proton-neutron concept of the nuclear structure will be necessary to understand the elementary

aspects of this subject. The composition of some of the nuclei are given in Table 1.1.

Table 1.1. The composition of the nuclei.

Elements	*Symbol*	*At. Wt.*	*At. No.*	*No. of Protons*	*No. of Neutrons*
Hydrogen	H	1.008	1	1	0
Helium	He	4.003	2	2	2
Lithium	Li	6.940	3	3	4
Beryllium	Be	9.013	4	4	5
Boron	B	10.820	5	5	6
Carbon	C	12.010	6	6	6
Nitrogen	N	14.008	7	7	7
Oxygen	O	16.000	8	8	8
Fluorine	F	19.000	9	9	10
Neon	Ne	20.183	10	10	10

Isotopes

The atomic weights of the various elements in Table 1.1 are not at all whole numbers. This has been found to be due to the fact that most elements are composed of mixtures of two or more kinds of atoms of different atomic masses, but similar in chemical properties. For example chlorine, with an atomic weight of 35.46, is composed of two kinds of chlorine atoms containing masses 35 and 37. But both types of the atoms of chlorine have atomic number 17. This means that both have 17 protons in the nucleus. The difference is, therefore, due to the number of neutrons in the nuclei of the different types of atoms. Chlorine 35 has 18 neutrons and chlorine 37 has 20 neutrons. The atoms having the same atomic number but different atomic masses are called *isotopes*. The only difference in the composition between different isotopes of the same element is in the number of neutrons in the nucleus. These isotopes, as a rule, occupy the same place in the periodic classification of elements. It is to be remembered that the atomic weight of an element is an average of the weights of the isotopes of element in the proportions in which they normally occur in nature. The atomic weight of chlorine 35.46 indicates that the atoms of isotopic weight or mass number 35

are more abundant than the isotope of chlorine having mass number 37. Isotopes of an element are generally written by the following symbols :

$_{17}Cl^{37}$	$_{1}H^{1}$	$_{20}Ca^{40}$
$_{17}Cl^{35}$	$_{1}H^{2}$	$_{20}Ca^{42}$
	$_{1}H^{3}$	$_{20}Ca^{44}$

The subscript stands for the atomic number of the element and the superscript denotes the mass number. There are more than 1,000 isotopes, natural and artificial, that have been identified of the known elements.

Atomic Spectra and Electronic Structure

The present-day knowledge of the structure of atom, particularly as regards the arrangements of extra-nuclear electrons is based upon the spectrum analysis and the lines which appear in them. When white light is passed through a glass prism, diffraction occurs and the white light becomes separated into its component coloure known as spectrum. Light consists of waves which is transverse. Of the visible colours, red has the greatest wavelength and violet, the shortest. The region between red to violet constitutes the visible region of the spectrum. But there are lights of greater wavelengths beyond the visible red and constitute the invisible infra-red region of the spectrum. Similarly there are

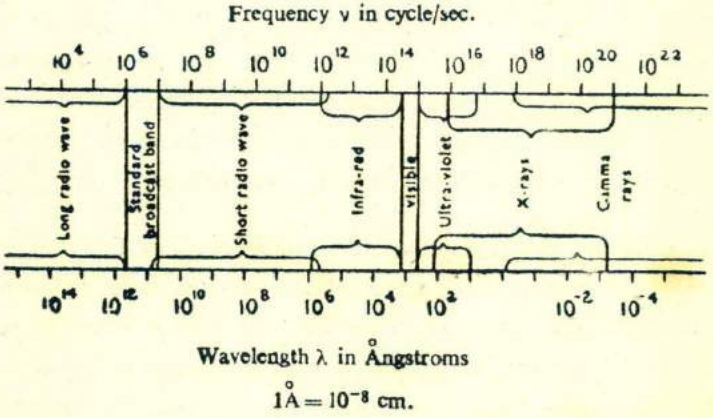


Fig. 1—8. Different regions of the spectrum.

lights of shorter wavelengths beyond the visible violet and constitute the invisible ultra-violet region of the spectrum. These invisible regions i. e., the infra-red and ultraviolet regions may be detected and recorded photographically. The different regions of the spectrum are shown in Fig. 1—8.

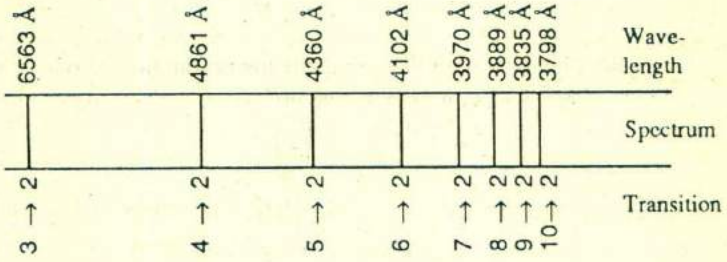
When a solid in heated to incandescence, it gives more or less a continuous spectrum. But gases and vapours under the same conditions or when subjected to electric discharge in a vacuum tube give spectrum often consisting of lines and bands occupying definite positions, i. e., with definite wavelengths. Thus we have "line spectra" and "band spectra". It was later shown that the line spectra are due to atoms and the band spectra are due to molecules.

It is from the atomic spectra consisting of sharp lines that informations regarding the extra-nuclear electrons are obtained. Many attempts have been made to explain how an excited atom radiates energy and why it radiates the particular wavelength or frequencies. Why the lines in the spectrum are sharp and well-defined?

It was also known that an element in the excited state, i. e., heated condition, in flame, during passage of electricity, subjected to electric arc or spark, exposure to exciting radiation etc. gives bright lines corresponding to the colours of the region in the visible spectrum. This is called "emission spectrum". But if white light is passed through the same element (gas or vapour) that is not glowing, the spectrum shows dark lines exactly at the same position characterised by the wavelengths where bright lines are obtained under excited conditions. The spectrum with dark lines is called "absorption spectrum".

Bunsen and Kirchhoff discovered that any given spectral line defined by its wavelength (or frequency) is characteristic of a type of atom, so that one may detect by means of an spectroscopic analysis what element is present in a given sample. The interpretation of Fraunhofer lines in the solar spectrum had led to the belief that absorption spectra or dark lines are caused by the presence of various elements in the sun, such as H, He, Na, Mg, Ca, Fe, etc.

In 1885, Balmer studied the hydrogen spectrum in the visible region and accurately measured the wavelengths of all the lines. The series of lines in the



Wavelengths in angstroms

Fig. 1–9 Balmer series spectrum of hydrogen in the visible region.

spectrum is known as Balmer series (Fig. 1—9). The values of the wavelengths so obtained by Balmer remarkably fitted into a general equation

$$\lambda = K \frac{n^2}{n^2 - 4}$$

where λ = wavelength and n is an integer greater than 2 and K is a constant.

The modified form of the equation is,

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

$$\text{or, } \bar{\upsilon} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

where $\bar{\upsilon}$ is the reciprocal of wavelength, i. e., $\frac{1}{\lambda}$ and is known as wave number, R is a constant known as Rydberg Constant named after its discoverer and represents a fundamental wave number and is very nearly the same for all elements, n is an integer and has values 3, 4, 5 etc. for the first, second, third etc. line in the hydrogen spectrum (represented as Hα, Hβ Hγ etc.).

The wave number $\bar{\upsilon}$ is also related to the frequency υ by the relationship $\upsilon = \bar{\upsilon}.c$, where c is the velocity of light (3×10^{10} cm. per second). The

frequency υ is the number of vibrations (wavelengths) per second whereas the wave number $\bar{\upsilon}$ is the number of vibrations (wavelengths) per centimetre.

Similarly, Lyman in 1906 studied the ultraviolet region of the hydrogen spectrum and observed a number of lines, having the wavelengths in excellent agreement with the equation,

$$\bar{\upsilon} = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$$

Where n is an integer having values 2, 3, 4, 5 etc. The series of lines in the ultraviolet region of the hydrogen spectrum is known an Lyman series. In 1908, Paschen discovered the series of lines in the infra-red region of the hydrogen spectrum and a general equation was also derived in which the Paschen series of lines fitted remarkably well. This equation follows the same pattern,

$$\bar{\upsilon} = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$$

Where n is an integer having values 4, 5, 6, etc.

All the above three equations can be further generalized and expressed by a single equation for all the series of lines in the hydrogen spectrum :

$$\bar{\upsilon} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\text{or, } \upsilon = Rc\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (\because \upsilon = \bar{\upsilon}\,.\,c)$$

Where c is the velocity of light, n_1 and n_2 are integers. These equations are all empirical. Rydberg constant and the equations were discovered merely by observation, calculation and hunting for a general rule.

The interpretation of the regularity and remarkable generalization was given for the first time by the theory of Bohr in 1913.

Limitations of Rutherford Atom Model

According to Rutherford, the nuclear model of atom consists of a positively charged nucleus, containing practically all the mass surrounded by a planetary system of electrons. The negative charges of the electrons are equal to the positive charges on the nucleus. It is also necessary to assume that the electrons

are in rapid motion about the nucleus so that the attractive electrostatic force of the nucleus is exactly counterbalanced by the outward centrifugal force produced by the motion of electrons. Obviously this picture of the atom is based upon Newton's Laws of motion and gravitation. Bohr pointed out that the Rutherford atom model is extremely unstable for the following reasons :-

(1) Newton's Laws of motion and gravitation can only be applied to neutral bodies such as planets and not to charged bodies such as tiny electrons moving round a positive nucleus. The analogy does not hold good since the electrons in an atom repel one another, whereas planets attract each other because of gravitational forces. Besides, there is electrostatic attraction in a nuclear atom model.

(2) According to Maxwell' stheory, any charged body such as electrons rotating in an orbit must radiate energy continuously thereby losing kinetic energy. Hence the electron must gradually spiral in towards the nucleus. The radius of the electron will gradually decrease and it will ultimately fall into the nucleus, thus annihilating the atom model.

(3) since the process of radiating energy would go on continuously, the atomic spectra should also be continuous and should not give sharp and well-defined lines.

In order to overcome these difficulties Bohr made some revolutionary suggestions in an attempt to arrive at a solution. He succeeded to some extent in correlating the empirical knowledge of atomic spectra and Planck's theory of radiation. According to Planck's theory of radiation, energy is radiated or absorbed by a body discontinuously in a definite fundamental unit or in an integral multiple of the fundamental unit. This unit of energy was called by Planck "a quantum". The magnitude of the unit of energy depends upon the frequency of rediation and thus a quantum of energy is directly proportional to the frequency of the radiation υ. In equation form this is expressed as,

$$E \propto \upsilon$$

$$\text{or, } E = h\upsilon$$

This quantum of energy is known as photon resulting from one electronic transition. E is the unit of energy and h, the Planck's constant. To convert

frequency υ to the equivalent energy in ergs, Planck used a conversion factor of 6.62×10^{-27} erg. sec. This factor is called 'h'. Thus the radiation of energy from a body will take place discontinuously in the unit hυ or a simple multiple of hυ, i. e., nhυ, where n is an integer (1, 2, 3, 4 etc.).

Bohr's Atom Model

Bohr constructed a theory of hydrogen atom in particular and to some extent of atomic structure in general. Bohr's theory consists of the following postulates :-

1. Postulate of Energy Levels

(a) An atom has a number of stable orbits in which an electron can revolve without the radiation of energy. These orbits are referred to as "Energy Levels". The electrons in these orbits possess an integral multiple of the quantum of energy i, e., hυ, but do not radiate it.

(b) If the electron moves in a circular orbit, its motion is subject to the ordinary laws of electrical and centrifugal forces. These orbits are decided by the condition that the angular momentum of the electron in such orbits must be an integral multiple of $\frac{h}{2\pi}$, that is,

$$mvr = n.\frac{h}{2\pi},$$

Where m is the mass of the electron, v is its velocity, r is the radius of the orbit and n is 1, 2, 3, 4, 5 etc. (h is the Planck's constant).

2. Postulate of Frequency or Radiation

According to this postulate an electron can, however, jump from one orbit to another. An atom radiates energy as light only when an electron passes from a higher energy level to another of lower energy giving definite spectral lines in emission spectra. The jump of an electron from a lower energy level to that of a higher energy level is manifested by absorption of energy giving dark lines. The quantity of energy radiated or absorbed is equal to the difference between the energies the atom possessed before and after the electron changed orbits.

If E_1 and E_2 are the energies of the electron in the initial and final levels respectively, the difference of energy radiated when the electron passes from the higher to the lower energy level is given by the relation :

$$E_2 - E_1 = h\upsilon,$$

where h is the Planck's constant and υ is the frequency of radiation.

On the basis of his theory, Bohr was able to account satisfactorily for the bright lines in a number of different atomic spectral series particularly in that of hydrogen.

The angular momentum of the electron is defined as the product of the velocity (v) of the electron in its orbit, mass (m) and radius of its orbit (r), i. e., $m\omega = mvr$ (Fig. 1-10), where ω is the angular velocity.

According to Bohr's postulate the angular momentum must be a simple multiple of $\frac{h}{2\pi}$ that is, $mvr = n\frac{h}{2\pi}$ where n has values 1, 2, 3, etc. and is

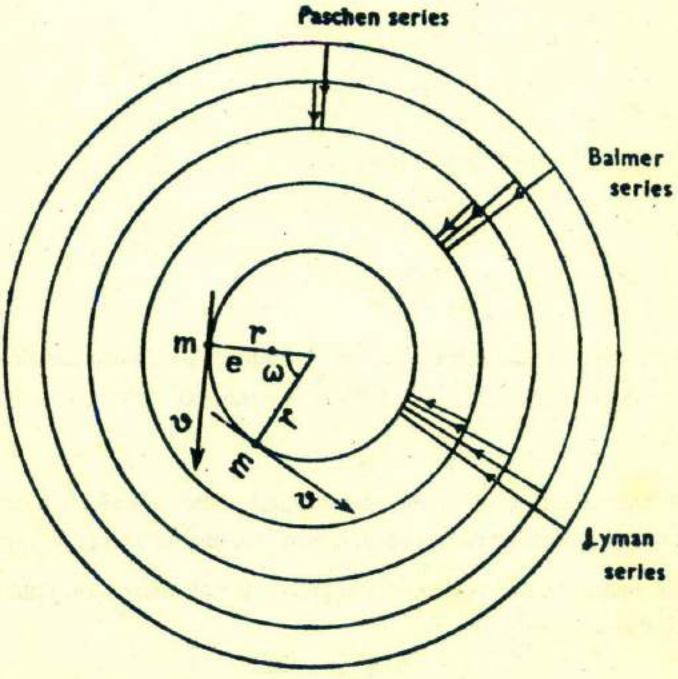


Fig. 1–10. Bohr hydrogen atom. Origin of spectral lines.

referred to as "quantum numbers". The total energy of the electron in an orbit is made up of kinetic and potential energies and can be calculated by applying the laws of mechanics and electrostatic forces of attraction. For an electron in an orbit of radius r, the electrostatic force of attraction between the nucleus with charge Z. e (where Z is the atomic number) is given by $\frac{Z.e^2}{r^2}$ This attraction is counterbalanced by the centrifugal force $\frac{mv^2}{r}$ (Fig. 1—10). Thus :

$$\frac{mv^2}{r} = \frac{Z.e^2}{r^2}$$

$$\text{or,} \quad v^2 = \frac{Z.e^2}{mr} \qquad \ldots\ldots \quad \ldots\ldots \quad \ldots\ldots \quad (1)$$

Bohr's postulate gives the quantum condition in which

$$mvr = n \cdot \frac{h}{2\pi}$$

$$\text{or,} \quad v = \frac{nh}{2\pi mr}$$

$$\text{or,} \quad v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \qquad \ldots\ldots \quad \ldots\ldots \quad \ldots\ldots \quad (2)$$

Combining the equations (1) and (2),

$$\frac{n^2h^2}{4\pi^2m^2r^2} = \frac{Z.e^2}{mr}$$

$$\text{or,} \quad r = \frac{n^2h^2}{4\pi^2m.Z.e^2} \qquad \ldots\ldots \quad \ldots\ldots \quad \ldots\ldots \quad (3)$$

solving the equation for n = 1 for hydrogen, (Z = 1), the radius of the first orbit, r = 0.53 x 10^{-8} cm., or = 0.53 $\mathring{A}$ is obtained (10^{-8} cm. = 1 angstrom unit, $\mathring{A}$).

The total energy E of an electron is equal to the sum of the kinetic energy (K. E.) and the potential energy (P. E.). Now, the kinetic energy = $\frac{1}{2}$ mv^2 and the potential energy of an electron of charge Z. e at a distance r from the nucleus is given by the equation :

$$\text{P. E.} = -\frac{Ze^2}{r}.$$

The total energy E of an electron in any orbit is given by the equation:

$$E = K.E. + P.E.$$

$$E = \frac{mv^2}{2} - \frac{Ze^2}{r}$$

Since, $$\frac{mv^2}{r} = \frac{Ze^2}{r^2}$$

therefore, $$E = \frac{Ze^2}{2r} - \frac{Ze^2}{r} = -\frac{Ze^2}{2r}$$

Substituting the value of r from (3) we get,

$$E = -\frac{2\pi^2 Z^2 e^4 m}{n^2 h^2} = -\frac{13.6}{n^2} \quad \text{electron volts} \ldots\ldots\ldots (4)$$

Where E is the total energy of the electron in the orbit designated by the quantum number n, e is the charge and m, the mass of the electron, Z is the number of electrons involved or the atomic number and this is 1 in the case of hydrogen atom, h is the Planck's constant.

Thus $E_1 = -13.6$ ev, $E_2 = -\frac{13.6}{2^2} = -\frac{13.6}{4} = -3.4$ ev

According to Bohr's postulate when an electron passes from one orbit to another of lower energy, radiation of energy occurs having the energy equal to the energy difference between the initial and final orbit or levels. If E_2 is the energy of the higher level and E_1 that of the lower level, the difference may be expressed as,

$$E_2 - E_1 = h\upsilon$$

The difference of the total energy of an electron in the orbits n_1 (using equation 4) may be shown by the equation,

$$E_2 - E_1 = h\upsilon = \frac{2\pi^2 Z^2 e^4 m}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Therefore, $$\upsilon = \frac{2\pi^2 Z^2 e^4 m}{h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right),$$

where μ is the frequency of radiation in cycles/second.

The difference in energies of the first level and second level, $E_2 - E_1 = -3.4 - (-13.6) = 10.2$ electron volts.

Since $\upsilon = \bar{\upsilon}\, c$, therefore, $\bar{\upsilon} = \frac{2\pi^2 Z^2 e^4 m}{h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

All the terms in $\frac{2\pi^2 Z^2 e^4 m}{h^3 c}$ are constant ; Z, the number of positive charges on the nucleus, is 1 in the case of hydrogen atom.

The value of $\frac{2\pi^2 Z^2 e^4 m}{h^3 c}$ for hydrogen has been calculated to be $=109{,}737.31 cm^{-1}$. This value is the same as found for Rydberg constant in the equation $\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$. Since wave number $\bar{\upsilon} = \frac{1}{\lambda}$. hence the relation becomes :

$$\bar{\upsilon} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

This equation is identical with the general equation for the wave number of any spectral line in all the region of the spectral series of the hydrogen atom. This discovery was perhaps, the most sensational evidence in favour of Bohr's theory when it was first published.

Origin of spectral Lines : The electron in the hydrogen atom exists normally in the *ground state* or lowest energy level when n_1 or $n = 1$, i. e., nearest to the nucleus. If, however, the atom is excited, the electron will move to some higher energy level ; from this it will tend to drop back to the lowest energy level in the stable position if not ionized. This happens either directly or through intermediate steps. When the electron is returning form a higher energy level to a lower one, excess energy will be liberated as radiation of some definite frequencies according to Bohr's theory. This will give rise to emission spectra. The absorption spectra will be produced in the reverse way. Since the same orbits are involved, the same spectral lines will be observed in emission and absorption spectra.

Thus, for all the lines in the Lyman series, $n_1 = 1$ in the general equation $\bar{\upsilon} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$, and $n_2 = 2, 3, 4, 5$ etc. energies will be emitted or absorbed giving definite lines in the spectrum.

Hence according to Bohr's theory the Lyman series of lines in the hydrogen spectrum are produced when an electron jumps from any higher level to the lowest level. In excited atoms all the electrons will not be raised to the same

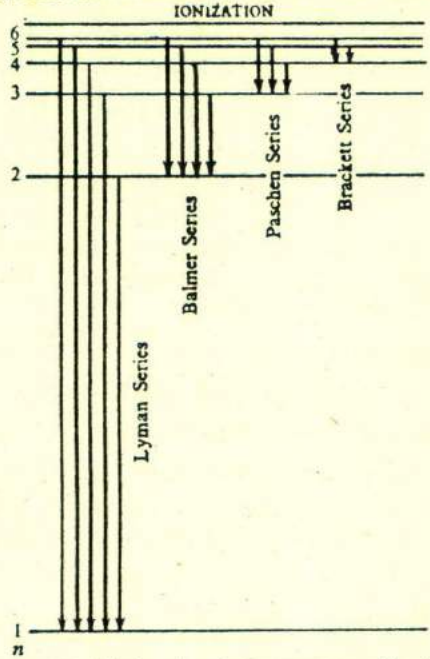


Fig. 1—11. Origin of emission spectra of hydrogen.

levels and consequently when these electrons fall back to the lowest level, a series of spectral lines will be produced as shown in Fig. 1—11. This happens in the ultraviolet region of the spectrum.

Similarly, the electrons in the various hydrogen atoms in the excited state will tend to fall back to the second energy level $n_1 = 2$ from outer levels. This takes place in the visible region and produces the Balmer series of lines. All electron transitions ending at $n_1 = 3$ from outer levels are indicated by Paschen series in the infra-red region. This theory, therefore, was remarkably successful in accounting for the main features of the hydrogen spectrum.

Limitations of Bohr Theory : As mentioned before, Bohr Theory was eminently successful in explaining the spectrum of hydrogen but failed to predict the energy states of more complicated atoms in which there are more than

one electron. Bohr presented a somewhat pictorial representation of the fact and is far from exact physical reality. Periodic motion around a central body usually follows an elliptic path rather than a circular path which has been assumed in the case of Bohr Theory. If electrons follow elliptical path, the velocity along the path does not remain constant. Fig. 1-12 indicates the precession of electron orbit due to changes in the velocity of the electron in elliptical orbit with the nucleus at one of the foci.

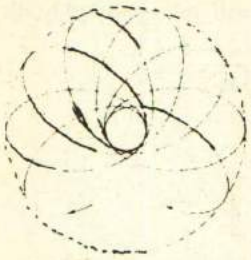


Fig. 1—12. Precession of the electron orbit due to changes in the velocity of the electron.

Moreover, according to Heisenberg, both the position and the momentum of an electron in an atom cannot be fixed simultaneously. This is known as Heisenberg's Uncertainty Principle. High resolving power spectroscope shows multiple lines in the atomic spectra and the multiplicity of lines has not been explained by Bohr Theory. Also the mass of an electron, m, moving with great speed v is not the same as the mass at rest, m_o and is given by the equation,

$$m = \frac{m_o}{\sqrt{1 - \frac{v^2}{c^2}}}$$

where c is the velocity of light.

when $v = c$. then $1 - \frac{v^2}{c^2} = 0$ and the rest mass $m_o = 0$. This is the case with photon which has the rest mass zero but other material particle has a real rest mass.

Quantum Numbers

The Principal Quantum Number : The nuclei of the more complex atoms are surrounded by orbital electrons which are arranged in a series of energy levels or spherical shells concentric with the nucleus. These electrons are classified in terms of their energy levels. One of the original assumptions of the Bohr theory was to fix the motion of an electron in a circular orbit with angular momentum equal to a simple multiple of $\frac{h}{2\pi}$, i.e., $mvr = \frac{n.h}{2\pi}$. the integer n is

designated as the Principal Quantum Number and represents any particular circular orbit. The value of n gives roughly the binding force and distance between the nucleus and the electron. This quantum number represents the size of the electron orbit. When $n = 1$, it represents the first energy level ; $n = 2$ represents the second energy level and so on. The first energy level is the one nearest the nucleus.

The Subsidiary Quantum Number : Sommerfeld modified the Bohr atom by adding elliptical orbits in order to explain the fine structure of the spectral lines. According to this modification the electrons in any particular energy level could have either a circular orbit or a number of elliptical orbits about the nucleus. Only those elliptical orbits are selected in which the electron possesses the angular momentum given by the equation

$$mvr = \frac{h\sqrt{l(l+1)}}{2\pi}$$

where l stands for subsidiary or azimuthal or orbital quantum number. This gives a measure of the angular momentum of an electron in its orbital motion about the nucleus.

Thus the subsidiary quantum numbers describe the shapes of the electron's orbit. The main energy level (or shells) of electron may be considered as being made up of one or more sub-levels (sub-shells). The number of sub-levels are limited by quantum condition so that if n is the principal quantum number, then the number of sub-levels will be equal to n. For $n = 3$, the number of possible sub -levels are 3. The term l may have values from 0 to $n-1$ Hence for the first energy level where $n = 1$, l can have only a value of 0. This means that energy level and sub-level coincide with each other. For $n = 2$, l can have values 0 and 1. Thus the second energy level has two sub-levels. Since the values of l in the mathematical treatment gives the shapes of the orbit, the orbits are circular when $l = n-1$ and have elliptical shapes when l is different from n—1. Fig. 1—13 shows the orbits with $n = 4$.

The Magnetic Quantum Number : Zeeman in 1896 observed the splitting of spectral lines in a magnetic field. This is known as Zeeman effect.

The third quantum number was introduced to explain the orientation of electronic arbit in space particularly under the influence of an applied magnetic

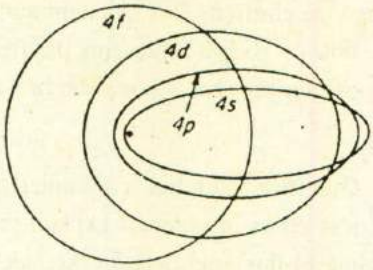


Fig. 1—13. Bohr-Sommerfeld orbits for principal quantum number $n = 4$.

field. This is known as the magnetic quantum number and is designated by m. The magnetic quantum knumber is associated with the translational motion of the electron in the atom. The values of m, i. e., the number of possible orientations depends to an extent upon the shape of the electron level. Mathematically, the magnetic quantum number may be expressed by the equation:

$$\text{Total angular momentum} = \frac{mh}{2\pi},$$

when m can have values from $-l$ to $+l$ including 0. Thus, when $n = 1$, then $l = 0$ and m can have only one value of 0. When $n = 2$, l can have values 0 and 1, and therefore, when $l=0$, m is also 0 and for $l=1$, m can have value -1,0 and +1.

The Spin Quantum Number : Stern and Gerlach (Fig 1—14) found that atoms having odd number of electrons such as H, Li, Na, Cu etc. possessed

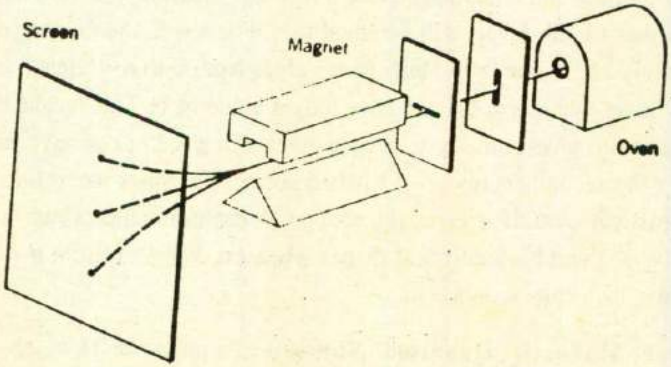


Fig. 1—14. Stern-Gerlach Experiment

magnetic moments caused by the spin of the electrons about their axis. The spin quantum number represents the direction of the electron spin and is denoted by s. The direction of spin is investigated in presence of external magnetic field and it is found that all electrons spin either in one direction (say, clockwise direction) or in the direction directly opposite (anti-clockwise). Mathematically, the spin quantum number is defined by the equation :

$$mvr = \frac{h\sqrt{s(s+1)}}{2\pi}$$

Where mvr is the angular momentum and the spin quantum numbers can have values $+\frac{1}{2}$ or $-\frac{1}{2}$ which are the mathematical notations for the spin direction of the electrons. The spin of the electrons appears to be quantized and is limited to only two values, $+\frac{1}{2}$ and $-\frac{1}{2}$ for s (spin quantum number).

The Physical Significance of Quantum Number

Four quantum numbers are necessary to describe an electron in an atom. These quantum numbers in effect describe the electron orbit in terms of (1) size, (2) shape, (3) orientation in space and (4) direction of spin of electron in its axis.

The principal quantum number, n, determines the size of the orbit and also gives a measure of the energy of the electron. The subsidiary quantum number, l, determines the shape of the orbit and indicates whether the orbit is circular or elliptical. The magnetic quantum number, m, determines the number of possible orientations in space or the number of planes in which the orbits are situated. The spin quantum number s stands for spin directions and the symbols $+\frac{1}{2}$ and $-\frac{1}{2}$ are mathematical notations of spin rather than that of physical rotation. Each electron going into an atom takes the four quantum numbers and has the lowest energy. This does not mean that all electrons in each of the elements should have values $n = 1$, $l = 0$ $m = 0$ and $s = \pm\frac{1}{2}$ which, in fact, are the lowest possible values of the four quantum numbers.

The principal and subsidiary quantum numbers representing the principal and secondary energy levels appear to be adequate descriptions of the energy states of an electron in isolated atoms. If the excited atoms from which electromagnetic radiation is being emitted is placed between the poles of a very powerful

magnetic field, a large increase in the number of different frequencies of radiation is observed. It is assumed that the secondary energy levels are further subdivided into other energy levels by the presence of magnetic field. These subdivisions of the secondary energy levels are called orbitals.

It is obvious that in the absence of a magnetic field the orbitals represent the same potential energy for an electron. A schematic diagram in Fig. 1—15 gives the resolutions of the energy levels to show the splitting of the spectral lines. It is to be noted that *s* energy levels are not split in a magnetic field, whereas

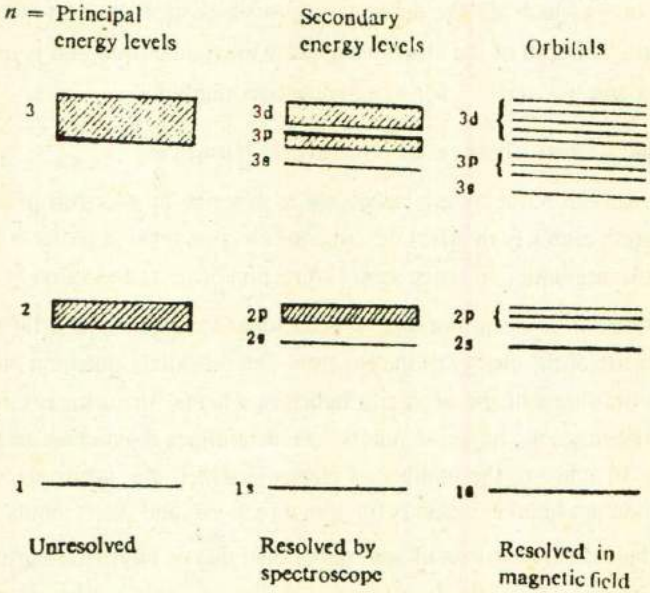


Fig. 1—15. Interpretation of spectral lines in magnetic field.

p type secondary levels appear to consist of three orbitals. The distribution of electrons in an atom is governed by the famous rule known as Pauli Exclusion Principle enunciated by W. Pauli in 1925.

Pauli Exclusion Principle : This principle may be stated in several ways, e. g.,

1. "No two electrons in the same atom can have the same values for the four quantum numbers."

2. "No two electrons in the same atom can have identical sets of four quantum numbers. "

3. "No more than one electron can have given values for the four Quantum Numbers."

The above rule appears to be analogous to the law : "Two bodies cannot be placed in the same position at the same time." Thus, two electrons of the same atom can have the same values for three of their quantum numbers, but the fourth quantum number must be different for the two electrons. Thus two electrons may have orbits of the same size, shape and orientation in space provided they have opposed spins. It is noted that each atomic orbital can hold a maximum number of two electrons provided their spins are opposed.

Types of Electrons : Based on the values of the quantum numbers the electrons are classified into **s. p. d** and **f** types. Electrons having subsidiary quantum numbers $l = 0, 1, 2, 3$ are called **s. p, d** and **f** electrons respectively. Thus, each value of l is represented by a different small letters.

Value of l	*Electron symbol*	*Maximum No. of electrons of each type*
0	**s**	2
1	**p**	6
2	**d**	10
3	**f**	14

The letters, **s, p, d** and **f** thus represent the possible sub-levels in addition to the principal quantum number. For instance, an electron having $n = 1$ and $l = 0$ is designated as 1s electron ; an electron with $n = 4$ and $l = 3$ is designated as 4f electron.

The maximum number of electrons in the various energy levels permitted by Pauli Exclusion Principle have been shown in Table 1. 2.

Table 1.2. Distribution of electrons on various energy levels based on quantum numbers.

Principal quantum number n	*Subsidiary quantum number l*	*Magnetic quantum number m*	*Spin quantum number s*	*Sub-total of electrons*	*Type of electron*	*Total number of electrons*
1	0	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$	2	s	2
2	0	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$	2	s	
	1	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		+1	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		−1	$+\frac{1}{2}$			
			$-\frac{1}{2}$	6	p	8
3	0	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$	2	s	
	1	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		−1	$+\frac{1}{2}$			
			$-\frac{1}{2}$	6	p	
		+1	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
	2	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$			

Contd.

Principal quantum number n	*Subsidiary quantum number l*	*Magnetic quantum number m*	*Spin quantum number s*	*Sub-total of electrons*	*Type of electron*	*Total number of electrons*
		+1	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		−1	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		+2	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		−2	$+\frac{1}{2}$			
			$-\frac{1}{2}$	10	d	18
4	0	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$	2	s	
	1	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		+1	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		−1	$+\frac{1}{2}$	6	p	
			$-\frac{1}{2}$			
	2	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		+1	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		−1	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		+2	$+\frac{1}{2}$			Contd.

Principal quantum number n	*Subsidiary quantum number l*	*Magnetic quantum number m*	*Spin quantum number s*	*Sub-total of electrons*	*Type of electron*	*Total number of electrons*
			$-\frac{1}{2}$			
		-2	$+\frac{1}{2}$			
			$-\frac{1}{2}$	10	d	
	3	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		$+1$	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		-1	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		$+2$	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		-2	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		$+3$	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		-3	$+\frac{1}{2}$			
			$-\frac{1}{2}$	14	f	32

Distribution of Electrons in the Atoms of Elements

As we proceed from one element to another beginning from hydrogen, the number of electrons in the atom increases by one in each instance. The electrons are not distributed at random but are arranged among the known elements in seven main energy levels designated by the quantum numbers $n = 1, 2, 3, 4, 5, 6$ and 7. These principal energy levels are divided into sub-levels indicated by s, p, d and f. The first energy level (n =1) which has only one sub-level is designated as 1s. The second energy level ($n = 2$) has two sub-levels designated

as 2s and 2p, the third ($n = 3$) energy level has three sub-levels designated as 3s, 3p and 3d and the fourth energy level $n = 4$ has four sub-levels 4s, 4p, 4d and 4f. The sub-levels are further divisible into orbitals. An s sub-level is made up of one orbital; a p sub-level-three orbitals; a d sub-level—five orbitals; and an f sub-level—seven orbitals.

Each electron orbital can accommodate a maximum of two electrons of opposed spins. Thus 1s orbital can hold a maximum of two electrons. The three p orbitals can hold a maximum of 6 electrons. These results are given in Table 1.3. The number in front of the sub-level symbol is the principal quantum number and the superscript is the number of electrons in the particular orbital.

Table 1.3. Electron distribution in orbitals.

Principal quantum number	*Maximum number of electrons*	*Number of electrons distributed in orbitals*
1	2	$1s^2$
2	8	$2s^2\,2p^6$
3	18	$3s^2\,3p^6\,3d^{10}$
4	32	$4s^2 4p^6 4d^{10} 4f^{14}$
5	32	$5s^2\,5p^6\,5d^{10}\,5f^{14}$

Thus the maximum number of electrons which the different types of atomic orbitals can accommodate are :

Sub-level	No. of orbitals	Total No. of electrons
s	1	2
p	3	6
d	5	10
f	7	14

In arriving at the electronic structure of atoms of the various elements, it is convenient to consider the sub-levels in which electrons would enter if these atoms were built up in the order of increasing atomic number, beginning with hydrogen. As each additional electron enters the atom, it will tend to occupy the available orbital of lowest energy. The higher orbitals are filled up only after lower energy orbitals have been completed.

The electron configurations of the elements are given in Table 1.4. Note that the electron configurations of chromium and copper and some other elements do not conform with the generalization stated above. In the case of chromium, the 3d level becomes half-filled (containing 5 electrons) and with copper 3d level becomes completely filled up with 10 electrons. The extra-

Table 1.4. Electron distribution in the atoms of the elements.

	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
H	1	1																	
He	2	2																	
Li	3	2	1																
Be	4	2	2																
B	5	2	2	1															
C	6	2	2	2															
N	7	2	2	3															
O	8	2	2	4															
F	9	2	2	5															
Ne	10	2	2	6															
Na	11	2	2	6	1														
Mg	12	2	2	6	2														
Al	13	2	2	6	2	1													
Si	14	2	2	6	2	2													
P	15	2	2	6	2	3													
S	16	2	2	6	2	4													
Cl	17	2	2	6	2	5													
Ar	18	2	2	6	2	6													
K	19	2	2	6	2	6		1											
Ca	20	2	2	6	2	6		2											
Sc	21	2	2	6	2	6	1	2											
Ti	22	2	2	6	2	6	2	2											
V	23	2	2	6	2	6	3	2											
Cr	24	2	2	6	2	6	5	1											
Mn	25	2	2	6	2	6	5	2											

Contd.

	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
Fe	26	2	2	6	2	6	6	2											
Co	27	2	2	6	2	6	7	2											
Ni	28	2	2	6	2	6	8	2											
Cu	29	2	2	6	2	6	10	1											
Zn	30	2	2	6	2	6	10	2											
Ga	31	2	2	6	2	6	10	2	1										
Ge	32	2	2	6	2	6	10	2	2										
As	33	2	2	6	2	6	10	2	3										
Se	34	2	2	6	2	6	10	2	4										
Br	35	2	2	6	2	6	10	2	5										
Kr	36	2	2	6	2	6	10	2	6										
Rb	37	2	2	6	2	6	10	2	6			1							
Sr	38	2	2	6	2	6	10	2	6			2							
Y	39	2	2	6	2	6	10	2	6	1		2							
Zr	40	2	2	6	2	6	10	2	6	2		2							
Nb	41	2	2	6	2	6	10	2	6	4		1							
Mo	42	2	2	6	2	6	10	2	6	5		1							
To	43	2	2	6	2	6	10	2	6	6		1							
Ru	44	2	2	6	2	6	10	2	6	7		1							
Rh	45	2	2	6	2	6	10	2	6	8		1							
Pd	46	2	2	6	2	6	10	2	6	10									
Ag	47	2	2	6	2	6	10	2	6	10		1							
Cd	48	2	2	6	2	6	10	2	6	10		2							
In	49	2	2	6	2	6	10	2	6	10		2	1						
Sn	50	2	2	6	2	6	10	2	6	10		2	2						
Sb	51	2	2	6	2	6	10	2	6	10		2	3						
Te	52	2	2	6	2	6	10	2	6	10		2	4						
I	53	2	2	6	2	5	10	2	6	10		2	5						
Xe	54	2	2	6	2	6	10	2	6	10	—	2	6						
Cs	55	2	2	6	2	6	10	2	6	10	—	2	6	—	—	1			
Ba	56	2	2	6	2	6	10	2	6	10		2	6			2			

Contd.

	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
La	57	2	2	6	2	6	10	2	6	10		2	6	1		2			
Ce	58	2	2	6	2	6	10	2	6	10	2	2	6			2			
Pr	59	2	2	6	2	6	10	2	6	10	3	2	6			2			
Nd	60	2	2	6	2	6	10	2	6	10	4	2	6			2			
Pm	61	2	2	6	2	6	10	2	6	10	5	2	6			2			
Sm	62	2	2	6	2	6	10	2	6	10	6	2	6			2			
Eu	63	2	2	6	2	6	10	2	7	10	7	2	6			2			
Gd	64	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
Tb	65	2	2	6	2	6	10	2	6	10	9	2	6			2			
Dy	66	2	2	6	2	6	10	2	6	10	10	2	6			2			
Ho	67	2	2	6	2	6	10	2	6	10	11	2	6			2			
Er	68	2	2	6	2	6	10	2	6	10	12	2	6			2			
Tm	69	2	2	6	2	6	10	2	7	10	13	2	6			2			
Yb	70	2	2	6	2	6	10	2	6	10	14	2	6			2			
Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
Ta	73	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
W	74	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
Re	75	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
Os	76	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
In	77	2	2	6	2	6	10	2	6	10	14	2	6	7		2			
Pt	78	2	2	6	2	6	10	2	6	10	14	2	6	9		1			
Au	79	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
Hg	80	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
Tl	81	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
Pb	82	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
Bi	83	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
Po	84	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
At	85	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
Rn	86	2	2	6	2	6	10	2	6	10	14	2	6	10	—	2	6		

Contd.

	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
Fr	87	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
Ra	88	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
Ac	89	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
Th	90	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
Pa	91	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
U	92	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
Np	93	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
Pu	94	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6		2
Am	95	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6		2
Cm	96	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
Bk	97	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
Cf	98	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2
En	99	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
Fm	100	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
Md	101	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2
No	102	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2
Lr	103	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2
Rf	104	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	2	2
Db	105	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	3	2
Sg	106	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	4	2
Bh	107	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	5	2
Hs	108	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	5	3
Mt	109	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	7	2

(N. B. The claims for the discovery and naming of the elements upto 112 are controversial.)

electrons needed for this arrangement appear to come from the 4s orbital, leaving it with only one electron. It has been shown that half-filled and completely filled energy levels represent conditions of stability. (See page 154)

Energy Level Diagram

A diagram representing roughly the energies of the electrons in the atoms is given in Fig.1-16. The energy of an electrons in an orbital is indicated by the vertical coordinate in the diagram. At the bottom, ls orbital of lowest energy and greatest stability has been given. Generally, the increasing electrons in the atom may be expected to occupy the orbitals in the order as they appear in the diagram. Each set of orbitals are being filled before electrons enter the next

higher orbitals. This scheme holds strictly only for the elements of low atomic numbers. The elements of higher atomic number have electron arrangements slightly different from that shown in the diagram. The relative energies of the higher orbitals do not change to the same extent.

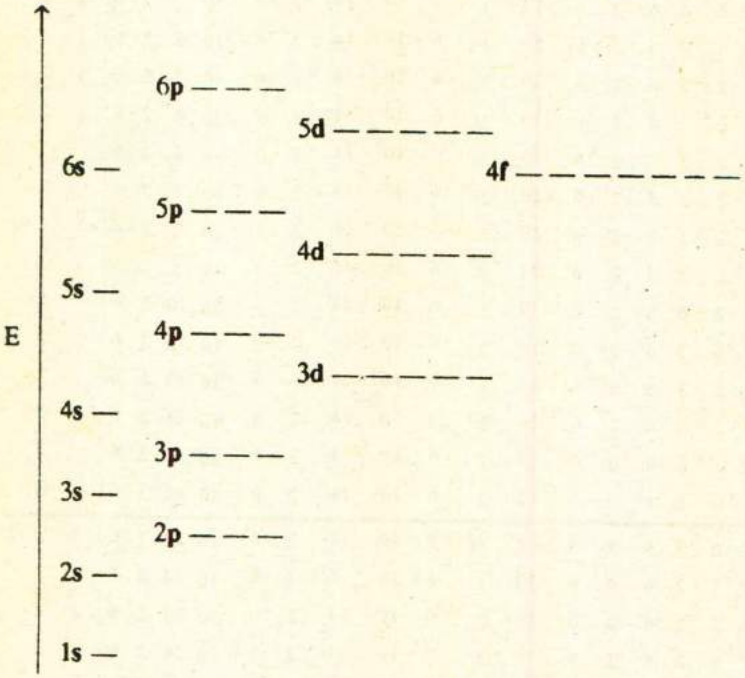


Fig. 1—16. Energy level diagram for atomic orbitals.

The above diagram may also be represented as follows to indicate the increasing energies of the atomic orbitals :

1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4f<5d<6p<6p<7s<5f<6d.

The order of filling of orbitals may be easily remembered by following the diagram in Fig. 1—17. Thus starting with 1s, proceed towards the head of the arrow and then start with the tail of the next arrow. The order of filling up is, therefore, 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f and 6d.

The inert gases have the electron configuration just before crossing the vertical line in Fig. 1-17 from right to left. The electron configurations of Cr

(24) ($1s^2\ 2s^2\ 2p^6\ 4s^1\ 3d^5$) and that of Cu (29) ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$) occur because of the irregularities due to extra stabilities of filled and half-filled

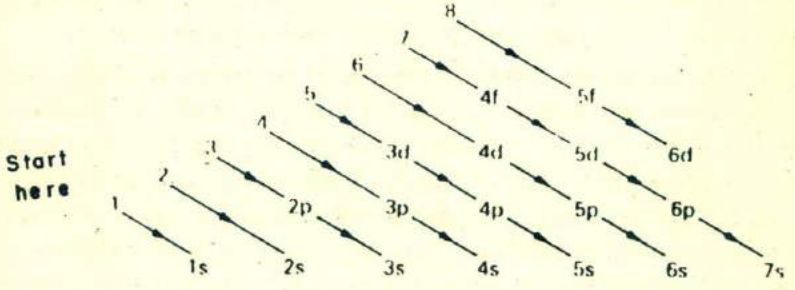


Fig. 1—17. Order of the filling of orbitals.

orbitals. The electron configuration of Ce (58) may be easily written as,

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^2$.

According to electronic configurations, four types of atoms can be easily distinguished :-

(i) Inert gases, He, Ne, Ar, Kr, Xe and Rn having outer group of electrons of considerable stability. These have complete s^2p^6 outer electron groupings except He ($1s^2$).

(ii) Atoms having all except the outermost electron groupings incomplete. These are alkali, alkaline earth metals etc. These have s^1 and s^2 electrons in the outermost levels respectively

(iii) Atoms having the two outermost electrons groupings incomplete. These include transition elements and d orbitals are being filled up.

(iv) Atoms having the three outermost electron groupings incomplete. These are rare-earth (lanthanides) and actinides in which mainly f electrons levels are being filled up.

Valence Electrons

It is to be emphasised that the electrons in the outermost orbital of an atom largely determine the chemical properties of the element. The electrons which are present in the outermost energy level of an atom are known as valence electrons

and these electrons determine the manner in which atoms combine with one another. Sodium metal is a very good conductor of electricity since the loose outer electron of sodium moves from one atom to the next giving rise to a flow of electrons through the sodium metal. In general, a metal is a good conductor of electricity because the valence electrons are comparatively lightly held by the atom and are free to move successively from one atom to the other.

Atoms having large number of electrons in the valence level have tendency to draw electrons to achieve stability. For instance, chlorine has 5 electrons in 3p orbital and takes up one electron to complete the 3p orbital having 6 electrons. In general, it may be seen that atoms having less than four electrons in the outer orbital tend to take up electrons. Generally it will be observed that elements classified as metals have tendency to give up valence electrons while non-metals usually take up electrons. Certain elements (metalloids) have both the tendencies of losing and gaining electrons and, therefore, exhibit the properties of both metals and non-metals.

Similarities of Structure

The electrons in the outermost energy level determine the chemical properties of the element. It is expected that group of elements having the same outer-configurations will exhibit quite similar chemical properties. It is for this reason that the groupwise chemical properties of, say, alkali metals, halogens etc. are similar. The electronic configurations of alkali metals, halogens and alkaline earth metals are given in Table 1.5.

Table 1.5. Electronic configurations of some chemically similar elements.

Elements	Atomic No.	Electronic configurations
Na	11	$1s^2\,2s^2\,2p^6\,3s^1$
K	19	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$
Rb	37	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}4s^2\,4p^6\,5s^1$
F	9	$1s^2\,2s^2\,2p^5$
Cl	17	$1s^2\,2s^2\,2p^6\,3s^2\,3p^5$
Br	35	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^5$
Be	4	$1s^2\,2s^2$
Mg	12	$1s^2\,2s^2\,2p^6\,3s^2$
Ca	20	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$

The Nature of Atomic Orbitals

Heisenberg Uncertainty Principle : The idea of fixed orbits of electron with fixed angular momentum is no longer acceptable, for, it is impossible to determine accurately both the exact position and the exact energy of an electron simultaneously. This is known as the Heisenberg Uncertainty Principle and maintains that the more accurately we measure the energy of a moving electron, the less accurately we can determine its position and vice versa. Therefore, the picture of an electron as a material particle of matter moving in a circular or elliptical orbit about a nucleus has little significance because such picture deals with great uncertainty as regards its position and momentum or its velocity. The best solution to this problem has been found in considering the electrons to possess the probability of being found at given location within the atom. An electron may be visualized to be in rapid motion in a relatively large region, spending most of its time in certain region of high probability, It is easier to imagine the electron as a cloud of negative charge with the cloud being dense in regions of high probability and more diffuse in regions of low probability. It is the electron clouds which are more appropriately called as *atomic orbitals*. The larger the number of the principal quantum number, the greater is the volume of the corresponding orbital. Thus a 2s electron has a larger orbital than a 1s electron, a 3s electron has a larger orbital than a 2s electron and so on. It may be noted, however, that outer orbitals and orbitals occupied by inner electrons in an atom do overlap and penetrate each other.

Wave Nature of Electrons :

The wave character of the electron was first suggested by L. de Broglie. He assigned a wavelength to the moving electron given by the equation,

$$\lambda = \frac{h}{mv},$$

Where v is the velocity and m is the mass of the electron, h is the Planck's universal constant (6.625×10^{-27} erg. sec) and λ is the wavelength. Experimentally the wave nature of electrons was established by the fact that crystals produce diffraction patterns similar to that produced by x-rays.

By the proposition of de Broglie, not only the electron is associated with wavelength λ, but also a photon of light has a mass m. Schrodinger incorporated the de Broglie concept in a wave equation describing the behaviour of electrons in atoms in terms of their wave nature, their energy states and their mass. This treatment ignores the fixed or restricted orbits of Bohr and Sommerfeld and allows the probability of finding each electron in a space around the nucleus.

An electron moving in a closed orbit is considered as describing a stationary or standing wave. In such electron wave Planck's equation applies so that energy E is directly proportional to the frequency υ or

$$E = h\upsilon \qquad \text{(h is the Planck's constant)}$$

Using Einstein's equation, $E = mc^2$, where m is the mass of photon moving with the velocity of light c, we have

$$mc^2 = h\upsilon$$

or $$mc = \frac{h\upsilon}{c} = \frac{h}{\lambda}, \qquad \text{since } \upsilon = \frac{c}{\lambda}$$

Hence $$\lambda = \frac{h}{mc}$$

Applying the above equation on electron moving with velocity v and associated with wavelength λ, the de Broglie relationship is obtained

$$\lambda = \frac{h}{mv}$$

An electron describing an stationary wave in an atom may be represented as in Fig. 1-18. If there are n number of wavelengths in the stationary wave in a

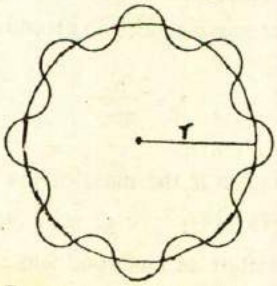


Fig. 1-18. Electron cloud of a stationary wave.

circle of circumference $2\pi r$ (r being the radius), then

$$2\pi r = n\lambda$$

or $$\lambda = \frac{2\pi r}{n}$$

Since de Broglie relationship gives

$$\lambda = \frac{h}{mv}$$

Therefore, $$\frac{2\pi r}{n} = \frac{h}{mv}$$

or $$mvr = n.\frac{h}{2\pi}$$

Thus the angular momentum, mvr, of an electron is an integral multiple of the quantity $\frac{h}{2\pi}$ which may be considered as the unit of angular momentum for the particle in motion describing the stationary wave around the nucleus.

According to the wave-mechanical calculations, the average distance from the nucleus and speed of an electron in any particular quantum orbit corresponds with that calculated by Bohr. But the angular momentum, however, is different. In particular, the electron in the normal quantum level is not moving around the nucleus with angular momentum $\frac{h}{2\pi}$, but is moving to and fro around the nucleus with zero angular momentum. The wave mechanical concept of the electron seeks to relate mathematically the energy, spin, momentum and other characteristics of the electron to the probability of finding the electron in a space around the nucleus.

Because atoms exhibit spherical symmetry, it is more convenient to represent electronic wave forms by polar coordinates r, θ and ϕ instead of the Cartesian co-ordinates x, y and z. The relationship between the two systems are shown in Fig. 1—19.

The relationship between the two coordinate systems is easily obtained as,

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta \quad \text{and} \quad r^2 = x^2 + y^2 + z^2$$

Instead of locating the electron in an orbit in three-dimentional directions as a function of x, y and z, it is covenient to represent the wave function Ψ, as a product of three functions Θ, Φ and R. that is,

$$\Psi = \Theta(\theta).\ \Phi(\phi).\ R.\ (r)$$

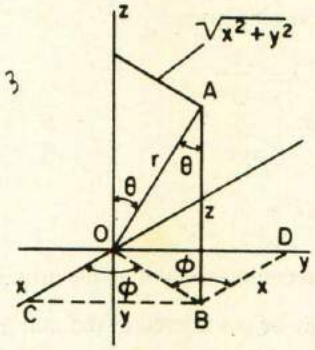


Fig. 1—19. The radial vector in three-dimensional space.

Where Θ is a mathematical expression of the variation of electron density as the angle θ varies. Φ is a mathematical expression of the change of electron density as the angle ϕ varies. R is a mathematical expression of the variation of electron density as the distance r increases to different distances from the nucleus of the atom.

Thus the behaviour of electron as a wave is described by a wave function represented by ψ. In the case of a standing wave described by an electron in an atom the probability of finding the electron at any point in an orbital is proportional to the square of its wave function, ψ^2. Mathematically, the probability $P = c^2\psi^2$, where c is a constant. Any event that is sure to occur is given a mathematical probability = 1. Hence the probability of the electron to be in its orbital is P = 1. Under this condition the orbital is *normalized*. The normalization of orbital is expressed by the function

$$c^2 \int \psi^2 dv = 1$$

Where dv = small increase in the volume of electron density and c = constant which, in this case = 1, Since $v = 4/3\ \pi r^3$, then $dv = 4\ \pi r^2 dr$. Hence

$$c^2 \int 4\pi r^2 \psi^2 dr = 1$$

If the separate orbitals in the same atom are normalized each containing one electron so that each orbital is independent, then the orbitals are said to be

orthogonal. Now, since atoms are considered to be spherical the electron density of any atomic orbital is represented as being in a spherical volume. Thus it is possible to sketch three-dimensional units of space within which the electron may, most probably, be found in a state corresponding to an orbital. In other words, it is in the space through which the charge of the electron is distributed in the orbitals in terms of the radial function and angular functions.

Alternatively, the electron may be imagined as a charged cloud carrying negative electricity and spreading over a relatively large area. The charged cloud is thick in region of high probability and more diffuse in low probability region. No experiment has yet been devised to prove or distinguish the above interpretation, although the "charge cloud" interpretation is more widely used.

There are various ways of representing electron charge cloud or probability of electron density around a nucleus. The simple hydrogen atom may be shown diagrammatically as in Fig. 1—20.

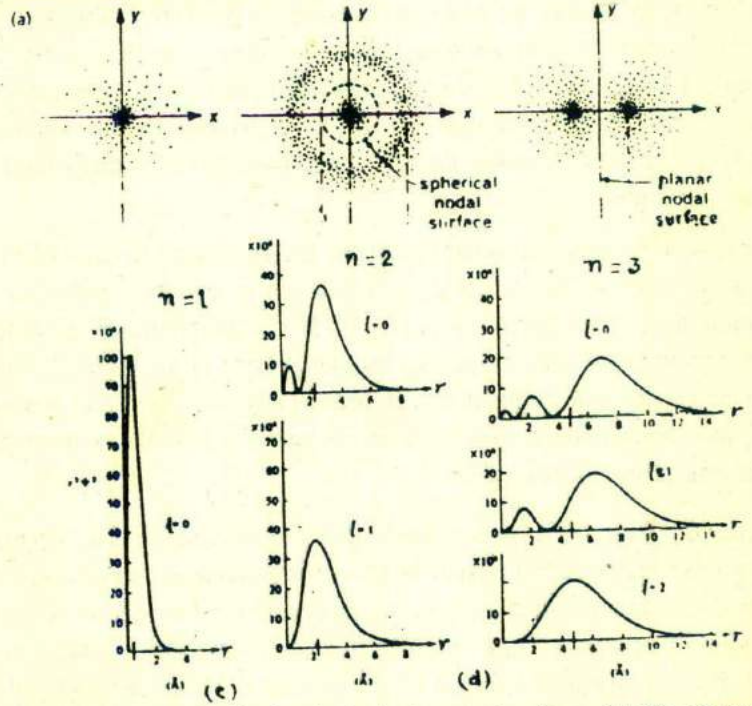


Fig. 1—20. Electron distribution in the hydrogen atom (n = 1). The charge cloud distribution (a). Probability density against distance from the nucleus (b). Probability density per unit volume against distance from the nucleus (c) The radial distribution of electron density for a 2s and 2p electrons (d).

The electron charge cloud has its greatest density nearest to the nucleus and becomes diffuse as the distance from the nucleus increases. Thus the probability of finding an electron in the hydrogen atom (s orbital, $n = 1$) is greatest in the small volume surrounding the nucleus in space. But there is also a finite probability that electron will be found away from the nucleus indicated by the diffuse dots in Fig. 1—20 (a). The same effect is represented in Fig. 1—20 (b) where the probability of electron density Ψ^2 has been shown graphically against the distance from the nucleus. The shape of the curve indicates that the electron is strongly attracted by the nucleus. When the electron charge cloud per unit volume $4\pi r^2\Psi^2$ is plotted against the distance from the nucleus, the probability is less close to the nucleus, since less space is available—attains a maximum point at a particular distance and then gradually falls off as the distance increases. This effect is represented in Fing. 1—20 (c) (for $n = 1$). In the case of hydrogen atom the total probability of finding an electron at all points (radially) is greatest when the distance from the nucleus, r, becomes equal to the Bohr radius. The plot shows a maximum at 0.53Å which is the Bohr radius for hydrogen atom. In the case of $n = 2$, as represented in Fing 1—20 (d), the two maxima correspond to the 2s energy level. However, the curve corresponding to 2p energy level has a single maximum.

Although the large maximum probability for locating an electron in the 2p level is closer to the nucleus than the maximum probability for finding the electron in the 2s level, as shown in Fig. 1—20 (d), an electron in the 2s level is at a slightly lower potential energy than an electron in the 2p level. This is due to the greater penetration of a 2s electron as compared to an electron in 2p level. Since there are three 2p orbitals, an electron in any one of the three states has the same probability disance.

Atomic Orbitals : It is possible to sketch three-dimensional patterns of space within which the electron may be found corresponding to an orbital. These are the spaces through which the electron moves over a long period of time or the charge of the electron is distributed in those spaces corresponding to the orbital. Thus the charge distribution for s type atomic orbitals are spherical and possess no directional characteristics because in these orbitals only the radial wave function is involved. It is more proper to consider the 1s charge distribu-

tion to be a hollow sphere with maximum of charge at a distance of $r = 0.53$ Å from the nucleus. The charge distribution for an electron in 2s orbital resembles two concentric hollow spheres with a minimum (node) in-between. But all the s type atomic orbitals are represented as a single sphere as shown in Fig. 1—21.

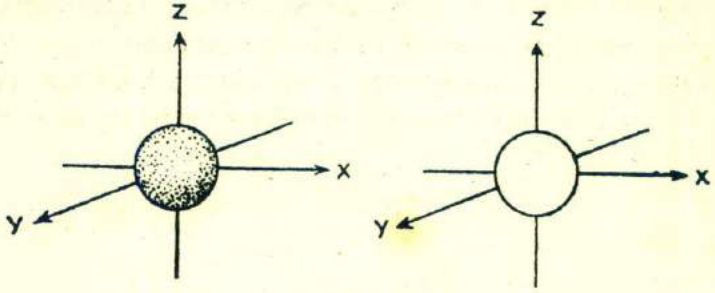


Fig. 1—21. Atomic s orbitals.

The charge distributions for electrons in p orbitals are directed in space and in terms of the Cartesian co-ordinates x, y and z-axes in such a way that the orbitals consist of two ellipsoids lying across each axis giving a dumb-bell shape. The directional characteristics arise because both the radial and angular wave functions are involved. The p orbitals are designated by subscripts p_x, p_y and p_z corresponding to x, y, z cartesian coordinates (Fig. 1—22).

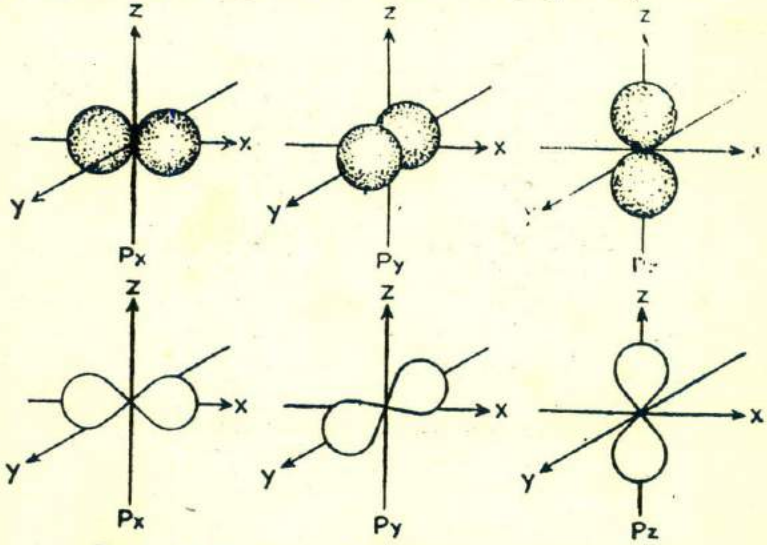


Fig. 1—22. Directional characteristics of atomic p orbitals.

The charge distribution corresponding to the five **d** orbitals are rather comples. Three of these consist of four lobes, each directed in between the axes xy, yz, and xz planes respectively. These are designated as d_{xy}, d_{yz} and d_{xz} orbitals. Another **d** orbital consists of four lobes directed along the x and y axes. This is designated as $dx^2\text{-}y^2$ orbital. The other **d** orbital consists of two lobes directed along z-áxis but is encircled by a ring of charge distribuüon in the xy plane. This is called d_z^2 orbital. The different **d** orbitals are shown in Fig. 1—23.

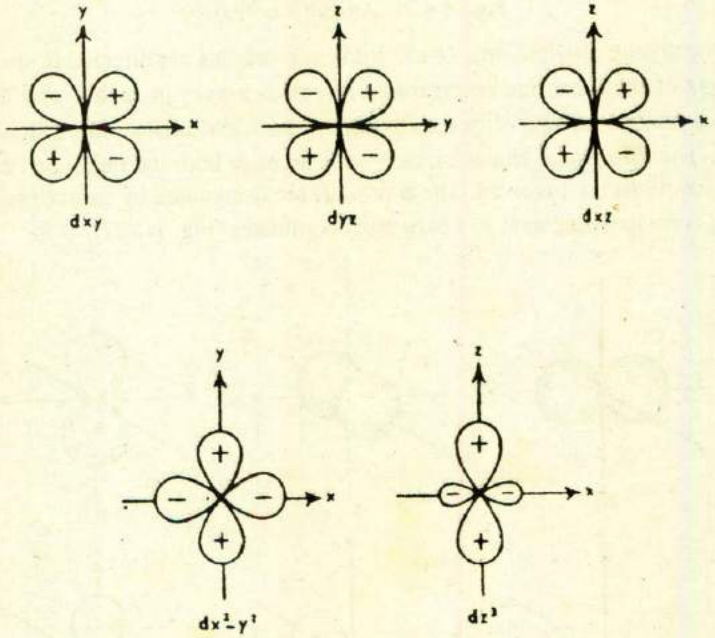


Fig. 1—23. Cross-section diagrams of **d** orbitals

THE SCHRÖDINGER EQUATION, THE QUANTUM NUMBERS AND ENERGY LEVELS

In 1926, Erwin Schrödinger developed an equation consistent with the wave properties of the electron. His basic equation was similar to an equation that is used to describe standing waves in general.

When the concepts of the Heisenberg uncertainty principle, the electron as a standing wave, and the de Broglie relationship are combined, the result is the wave-mechanical theory of the atom, expressed usually in the form of the Schrödinger wave equation :

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi+\frac{8\pi^2 m}{h^2}(E-U)\psi=O$$

E is the sum of the kinetic energy and the potential energy of the atom. U is the potential energy of the atom, m is the mass of the electron, h is Planck's constant, and ψ is the wave function describing the electron in a particular orbital. For example, the wave function for an electron in a 1s orbital is

$$\psi=\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2}e^{-r/a_o}$$

where a_o is the Bohr radius with n = 1) and r is any radius from the nucleus.

The differential $\dfrac{\partial^2}{\partial x^2}+\dfrac{\partial^2}{\partial y^2}+\dfrac{\partial^2}{\partial z^2}$

is a mathematical operation from the calculus. $\dfrac{\partial^2\psi}{\partial x^2}$, for example, is read, "the second derivative of ψ with respect to the x coordinate of a three-dimensional system". Performing this mathematical operation gives the change in the rate of change of ψ along the x coordinate.

Although to know the intricacies of the mathematics of the Schrödinger equation is important in checking the limitation of this model of the atom, perhaps more important here is to understand the utility of the theory in explaining chemical properties of matter.

Solving the Schrödinger equation yields energy levels and wave functions for electrons in particular orbitals in an atom, specifically in the hydrogen atom. Each orbital can contain a maximum of two electrons and is a different stable energy level which these electrons can have within the atom. The student should not

confuse these orbitals with the Bohr orbits. In the first place, the orbitals have nothing to do with the path of an electron; if an electron is in a particular orbital, this simply means that the electron has a particular energy and a probable location within the atom. But the orbital information does not specify the movement of the electron. In the second place, the energies of the orbitals are subdivisions of the energies of the Bohr orbits.

Probabilities of locating electron within an atom and quantum numbers are two properties of orbitals which emerge from the solutions of the Schrödinger equation. Quantum numbers are used to describe the energy and the assignment of an electron to possible orbitals within the atom. Probabilities give the chance of finding an electron at a given location within an atom. The actual solution of the Schrödinger equation involves rather sophisticated calculus and consequently, we shall not solve it.

Questions and Problems

1. How do you prove the existence of electrons in an atom?
2. Devise an experiment to show that electrons carry negative charges.
3. What is a proton and a neutron?
4. (a) Name three important fundamental particles of atom and give short description of each.

   (b) Explain the solar system atom model and construct models of the following atoms :-

   (i) Neon, (ii) Sodium, (iii) Beryllium.
5. How will you prove the presence of a nucleus in an atom?
6. Write short notes on :-

   (a) Atomic number ; (b) Nuclear charge.
7. What is meant by an excited atom? How could you excite an atom?
8. How will you define a Bohr atom model?
9. Explain energy levels of electrons in atoms.
10. What is the relationship between spectrum of an element and its atomic structure? What are quantum numbers?

11. Show the distribution of electrons in the atoms of Be (4), Mg (12) and Ca (20).

12. Give an account of the structure of atoms with reference to the arrangement of orbital electrons.

    Explain the term "Quantum numbers".

13. Why four quantum numbers are necessary to describe an electron in an atom?

14. What is the origin of the **s, p, d** and **f** types of electrons?

15. What is the maximum number of electrons in 5f and 3f energy levels?

16. Why hydrogen atom should give so many lines in its spectrum although there is only one electron in hydrogen atom?

17. Calculate the wavelength of Hα & Hβ using the round figure value of $R = 109,300\ cm^{-1}$.

18. What is Pauli Exclusion Principle? How does it govern the distribution of electrons in the atoms of H and Na?

19. Show the distribution of electrons in Ca (20) and Cr (24).

20. The atoms contain electrically charged particles, yet they are neutral. Explain.

21. What is meant by the following notations : $1s^1$, $2p^5$, $3d^0$, $4f^{10}$, $3p^3$ and $3d^5$?

22. What do you understand by the term "Isotopes"? How will you write symbolically the isotopes of chlorine and hydrogen?

23. Write a concise account of the modern concept of the structure of atoms with particular reference to the distribution of orbital electrons.

24. Why are four quantum numbers necessary to formulate the electronic configuration of atoms? Show the relations amongst them.

25. Write short note on Fundamental Particles.

26. Give an account of Quantum Numbers.

27. Write brief account of :
    (a) Bohr's concept of atomic model and the origin of spectra in a hydrogen atom.
    (b) Pauli Exclusion Principles.

28. (a) Give a brief account of the modern concept of the structure of atoms.
    (b) Explain the terms :
    Pauli Exclusion Principle; Quantum Numbers; Planck constant.

29. (a) What are quantum numbers? Indicate their significance. (b) Briefly discuss the principle for the building up of atoms in respect of the arrangements of extranuclear electrons. (c) Write the electronic configurations of Cr ($Z = 24$) and Ce ($Z = 58$).

30. Draw the sketches of p and d orbitals showing the directional characteristics.

31. For the proton and electron the e/m are respectively 2.88×10^{14} esu/g and 5.28×10^{17} esu/g. Calculate masses of the proton and electron.

32. Why has the Bohr model of the atom become outmoded ?

33. Calculate the wave length of light emitted from H for the electronic transition from energy level $n = 3$ to $n = 2$ using $R = 109600\ cm^{-1}$.

34. A bar of iron at high temperature is red. Is the light emitted from the glowing bar due to electrons moving from low energy to high energy or dropping from a high energy to lower energy levels ?

35. Derive relationships to show that frequency varies with energy and also wavelengths varies with energy.

CHAPTER 2

THE CHEMICAL BOND

The Concept of Chemical Bond

When it is considered that a molecule is formed by combination of two or more atoms either of the same or of different elements the question naturally arises as to what are the forces which ordinarily hold the atoms together in a molecule. Before the discovery of the electronic structures of atoms the nature of the forces holding atoms together in molecules or crystals was mysterious and generally chemical bond was considered to be formed due to the combining capacity of different elements with atoms of hydrogen or oxygen or chlorine. This combining capacity or "valency" was considered to be the number of other atoms with which an atom of an element can combine. The classical concept of chemical bond formation has been largely replaced by the electronic concepts and the modern progress in the field of structural chemistry presents a great landmark in the advancement of our knowledge regarding the structure of matter.

The Electronic Concept

The combination or joining together of two atoms, such as that of H to H_2 appears at the first sight a mysterious phenomenon, if not an impossible one, since both the atoms are electrically neutral and should not combine with each other because of repulsion between the electron clouds of the two H atoms.

It is to be remembered that electrons play a very important role in the formation of chemical bonds. These are the electrons in the outermost energy level which undergo rearrangement or regrouping to form more stable arrangement. The electronic concept of chemical bond was advanced by W. Kossel and G. N. Lewis in 1916 independently.

The Fundamental abilities of the atoms of various elements to combine with each other depend largely upon the extent to which their electron levels are

completed. It has been considered that since the inert gases are chemically inactive, the atoms of the elements containing a total of 2, 10, 18, 36, 54 and 86 extra-nuclear electrons apparently impart a greater electronic stability than elements intermediate between them.

As regards the electronic arrangements we have classified atoms into four groups : (i) Atoms with complete electronic groupings. (ii) Atoms having all but the outermost electronic trouping incomplete. (iii) Atoms having two outermost electron levels incomplete. (iv) Atoms with three outermost energy levels incomplete. This concept was based on inert gases' electronic configurations which have incomplete levels except He and Ne.

The inert gases with stable electronic configurations do not normally enter into chemical combination and have two electrons (in the case of He) and eight electrons (in the case of other inert gases) in the outermost electron levels. Therefore, these electron arrangements represent complete groupings. Electrons containing less than eight electrons in the outermost energy level are incomplete and belong to the second type. The third and the fourth type of atoms having two and three outermost electron groupings incomplete enter into chemical combination in a variety of ways which are discussed latter.

In effect, the following principles may be enunciated to understand the early electronic theory of chemical bonding.

Principles of Electronic Theory of Chemical Bond :

(1) Chemical combination between atoms of the same or different elements takes place due to the tendency by the outermost electron groups to attain the stable arrangement of inert gases.*

(2) The attainment of inert gas electron configuration may take place by complete transference of electrons from one atom to another. The resulting electrically charged atoms (or ions) are held together by electrostatic force of attraction. The chemical bond so formed is known as electrovalent or *ionic bond.*

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* It needs some extension because these also include other stable electronic groupings beside those of inert gases which is more generally applicable.

(3) The attainment of inert gas configuration may occur by sharing of electrons (in pairs) between two atoms. The chemical bond so formed is called *covalent bond.*

(4) The attainment of electron groupings of inert gases may also happen by both transference and sharing of electrons between atoms in pairs. The bond so formed is known as *coordination bond.*

The Ionic Bond

The ionic bond is formed when one or more electrons are transferred from one atom to the other to complete the orbitals in each case. In both cases, the electronic arrangements of the resulting ions is identical to that of an atom of one of the inert gases. Such elements are generally those which immediately precede and those which closely follow the inert gases in the periodic classification. Table 2.1 shows the electronic arrangements of neon and argon and some of the elements that immediately precede and follow them in the Periodic Table.

Table 2.1. Electronic arrangement of inert gases and adjacent elements.

Elements	*At. No.*	*Electron arrangement*
O	8	$1s^2\ 2s^2\ 2p^4$
F	9	$1s^2\ 2s^2\ 2p^5$
Ne	10	$1s^2\ 2s^2\ 2p^6$
Na	11	$1s^2\ 2s^2\ 2p^6\ 3s^1$
Mg	12	$1s^2\ 2s^2\ 2p^6\ 3s^2$
S	16	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
Cl	17	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p5$
Ar	18	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
K	19	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
Ca	20	$1s^2\ 2s^2\ 2p^6\ 4s^2\ 3p6\ 4s^2$

It is noted from Table 2.1 that the gas neon (Ne) has 8 electrons in its outer energy level. The sodium atom which follows neon has the electronic structure of neon plus an electron in the next higher energy level. When the sodium atom loses the extra electron, it would then have an electronic arrangement identical to

that of neon (2,8) and sodium atom will form positively charged ion because it has now 11 protons but 10 electrons. This may be represented more simply as,

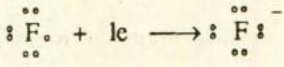
$$Na^{\circ}\ (1s^2\ 2s^2\ 2p^6\ 3s^1) - le \longrightarrow N\overset{+}{a}(1s^2\ 2s^2\ 2p^6)$$

the dot (°) in Na represents the single electron in the outermost level ($3s^1$)

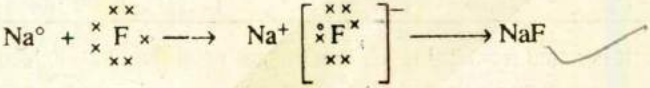
Similarly, the formation of negatively charged fluoride ior (F^-) from neutral fluorine atom F, having 7 electron in the outermost energy level and placed just before Ne in the Periodic Table may be illustrated as follows :

$$F\ (1s^2\ 2s^2\ 2p^5) + le \longrightarrow F^-\ (1s^2\ 2s^2\ 2p^6)$$

Thus the fluorine atom by entering into chemical reactions gains one electron and the electronic arrangement of the resulting fluoride ion (F^-) is identical to that of neon. The fluoride ion has one electron more than the fluorine atom :



Now, when a sodium atom and a fluorine atom are brought together, the sodium atom loses one electron to form a stable positive ion, Na^+, and the fluorine atom gains this electron to form a stable negative ion, F^-. The two ions Na^+ and F^- are now held together by the electrostatic force of attraction to for molecule of NaF. Thus the chemical bond formed between oppositely cha ions is known as ionic bond that hold the resulting compound. It is to be n that the transfer of electron from the electron cloud of sodium atom to the electron cloud of fluorine atom constitutes the chemical change represented by the equation,



Similarly, the bond between magnesium and oxygen in magnesium oxide (MgO) involves two electrons.

Mg	$1s^2\ 2s^2\ 2p^6\ 3s^2$	
Mg^{+2}	$1s^2\ 2s^2\ 2p^6$	(Neon structure)
O	$1s^2\ 2s^2\ 2p^4$	
O^{-2}	$1s^2\ 2s^2\ 2p^6$	(Neon structure)

$$\underline{{}^{\circ}Mg^{\circ}} + :\ddot{O}: \longrightarrow Mg^{+2} + :\ddot{\underset{\cdot\cdot}{O}}:^{-2} \longrightarrow MgO$$

Thus when magnesium atom enters into combination, it gives up 2 electrons to form a dipositive magnesium ion, Mg^{+2}, which has an electronic arrangement identical to that of neon. The oxygen atom by gaining two electrons becomes O^{-2} ion again having the neon arrangement. When magnesium and oxygen react with each other, two electrons are transferred from magnesium atom to oxygen atom and the resulting $Mg^{+2}O^{-2}$ or MgO are, therefore, held together by ionic bond.

Extending the arguments to other compounds such as CaS and KCl, it can be proved that Ca^{+2} and K^{+} assume the electronic configuration of argon (2, 8, 8) by losing 2 electrons and 1 electron respectively. The sulphur atom takes up 2 electrons and then has an electronic arrangement identical to that of argon. Chlorine atom gains 1 electron from potassium and has the electron configuration of argon. Hence in CaS, positive Ca^{+2} ion is combined to S^{-2} ion by means of ionic bond. Similarly, K^{+} ion and Cl^{-} ion combine by means of ionic bond to form KCl. In short, the electrovalent bond or ionic bond results from a coulombic attraction between the excess charges on the oppositely charged ions.

Similarly, K_2S and $CaCl_2$ may be represented as :

$$K^{+}\ K^{+}\ \left[\ {}^{\circ}_{\circ}\ddot{\underset{\cdot\cdot}{S}}\times\ \right]^{-2}$$

K_2S

$$Ca^{+2}\ \left[\ {}^{\circ}_{\times}\ddot{\underset{\cdot\cdot}{Cl}}\times\ \right]^{-}\qquad \left[\ {}^{\circ}_{\times}\ddot{\underset{\cdot\cdot}{Cl}}\times\ \right]^{-}$$

$CaCl_2$

The cations with inert gas configurations are generally those of the following metals.

Li^+,	Be^{+2}			He structure
Na^+,	Mg^{+2},	Al^{+3}		Ne structure
K^+,	Ca^{+2},	Sc^{+3}		Ar structure
Rb^+,	Sr^{+2},	Y^{+3},	Zr^{+4}	Kr structure
Cs^+,	Ba^{+2},	La^{+3},	Ce^{+4}	Xe structure

The anions having inert gas structure are mainly the halides, oxides and nitrides.

Halides	F^-	Ne structure
	Cl^-	Ar structure
	Br^-	Kr structure
	I^-	Xe structure
Oxides	O^{-2}	Ne structure
Nitrides	N^{-3}	Ne structure

Limitations of Ionic Bond.

(1) It is seen that there is a limit to gain and loss of electrons by an atom to form positive and negative ions mainly because of the energy considerations. When a neutral atom loses more than one electron, more work will be required to remove them against the attraction of positive nucleus. Similarly, gaining of successive electron makes the negative charge on the negative ion greater and thereby oppose the approach of further electrons. Thus F will form F^- but not F^{+7}; similarly, N^{+3} is formed but not isolated N^{+5}. Also C^{+4} and C^{-4} are normally not formed. Ions carrying high charges are rare because of the large amount of energy involved in electron transfer.

(2) Many cations do not always have inert gas structure. There are cations which have the outer $s^2\ p^6\ d^{10}$ structure instead of $s^2\ p^6$ groups. Thus

Cu^+, Zn^{+2}, Ga^{+3} have outer $3s^2\ 3p^6\ 3d^{10}$ groupings.

Ag^+, Cd^{+2} In^{+3}, Sn^{+4} have outer $4s^2\ 4p^6\ 4d^{10}$ groupings

Au^+, Hg^{+2}, Tl^{+3}, Pb^{+4} have outer $5s^2\ 5p^6\ 5d^{10}$ groupings

These are not much stable and show variable structures

Cu— $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

Cu^+— $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

Cu^{+2}—$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

Similarly, Ag^+, Ag^{+2}, Au^+ Au^{+3} etc. are also formed. Ag^+ and Au^{+3} are most stable cations in the group.

(3) The electron grouping $s^2\ p^6\ d^{10}$ in Zn^{+2}, Cd^{+2} and Hg^{+2} appear to be stable since no extra electron is lost from these cations.

(4) Transition metal cations show variable charge and do not have either inert gas $s^2\ p^6$ or 18 electron $s^2\ p^6\ d^{10}$ structures.

Fe— $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

Fe^{+2}— $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

Fe^{+3}— $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

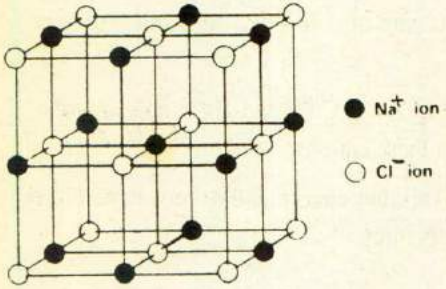
Similarly, Co^{+2}, Co^{+3}, Mn^{+2} etc. have variable charges.

General Properties of the Ionic Bond

Since the ionic bond results from the electronic attraction between the positive and negative ions, the strength of the bond so formed can be calculated roughly from the product of the charges on the ions and distance between the effective centres of the ions. The ionic bond is neither rigid nor directed. The electrostatic field of the ions extend in all directions. Consequently, a crystal of ionic compound is actually a cluster or aggregate of ions. The molecule is also called polar since it develops a positive and a negative pole or electrically charged ends separated by a finite distance. The following important properties of ionic bond may by mentioned:—

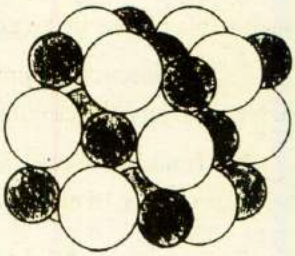
(1) Crystalline State : Ionic crystals are composed of cluster of ions in the crystal lattice or the atomic network and produce geometric shapes because of the arrangements of ions in space. For instance, in sodium chloride each sodium ion is surrounded by six choloride ions and each chloride ion is surrounded by six sodium ions in the cubic crystal lattice or atomic network in space. The proof is based upon the diffraction of x-rays produced by the crystals of sodium chloride.

This structure of sodium chloride has been shown in Fig. 2—1 and gives cubic crystals.



(a)

Fig. 2—1 (a) The crystal pattern of sodium chloride



(b)

Fig. 2—1 (b). The packing of the ions in sodium chloride.

(2) Electrical Conductivity : Ionic compounds either in the fused state or in solutions are good conductors of electricity. It may be easily visualized that in the fused state or in solutions, ions are dissociated and because the restraining forces of the crystal lattice are no longer present, the ions are free to move under the influence of electric field. Such solutions or melts are good conductors of electricity.

(3) Isomorphism : Ionic crystals having the same crystalline structures have been related to the electron arrangements of the ions in the solids. The different compounds containing ionic bonds have ions which assume the same electron arrangements in their molecules and hence show similar crystalline forms. For instance NaF is isomorphous with MgO, and K_2S has the same crystalline form as that of $CaCl_2$.

Na^+	$1s^2\,2s^2\,2p^6$	F^-	$1s^2\,2s^2\,2p^6$
Mg^{+2}	$1s^2\,2s^2\,2p^6$	O^{-2}	$1s^2\,2s^2\,2p^6$

Similarly, in the case of K^+, S^{-2}, Ca^{+2} and Cl^- ions, the electron groupings are identical.

(4) Dielectric Constant : When a dipolar or polar molecule is placed in an electrostatic field the positive end of the dipole is directed towards the negative pole of the electric field and *vice versa*. The oriented dipole oppose the

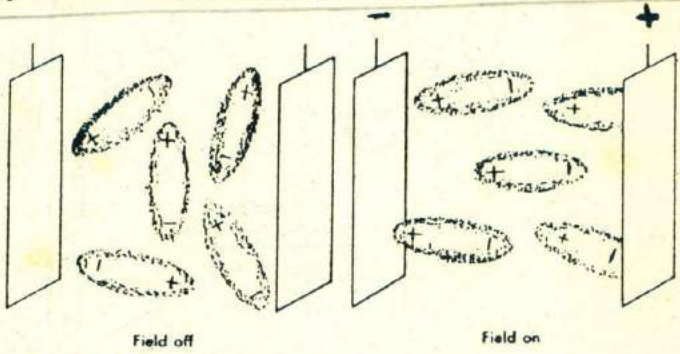


Fig. 2—2. Orientation of dipolar molecules in an electric field.

field and the intesity of the electric field is reduced. The reducing tendency is measured by the dielectric constant or the specific inductive capacity of the polar substance. The substances containing ionic bonds have high dielectric constant.

(5) Melting and Boiling Points : Molecules which possess dipoles may show a tendency to "dipole association" on account of mutual attractions of the opposite poles. Thus in the ionic crystals the ions exert a powerful electrostatic force on each other. The tendency to dipole association gives rise to "abnormal" behaviour in liquids and since the molecules with strong dipoles have stronger mutual attractions, a considerable amount of work is needed to separate them from one another. Thus it is natural to suppose that ionic compounds have high melting and boiling points. For instance, NaCl boils at 1470°C whereas the nonionic (covalent) CCl_4 bolis at 77°C only. It is to be noted that on heating. the kinetic energy of the particles within the solid is increased. The increased vibrations of the particles overcome the forces holding the particles together and they break away from their fixed positions.

(6) Reactivity : The reactions between ionic compounds generally take place with great speed, for instance, during the precipitation reactions in aqueous solution. Drastic methods are required to bring about reactions between non-ionic compounds.

(7) ***Solubility*** : Ionic compounds are generally more soluble in polar than in non-polar solvents. For instance, sodium chloride dissolves in water but

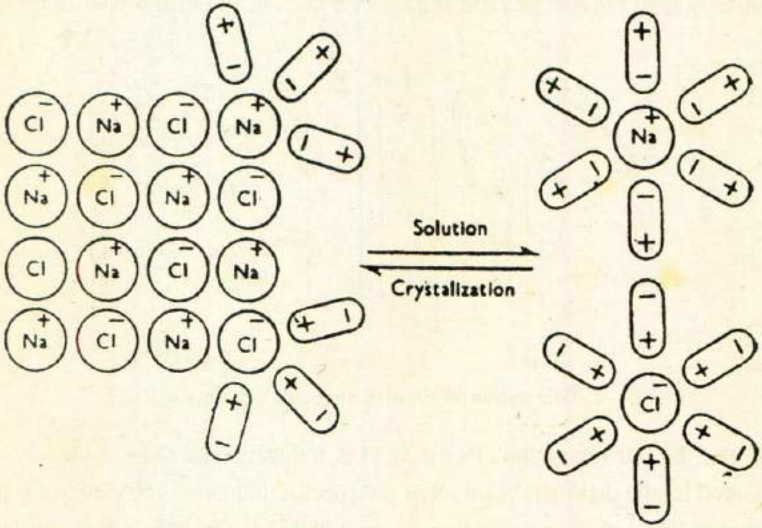


Fig. 2—3. Schematic diagram of the solution process of an ionic compound, NaCl.

not in benzene. Similarly, naphthalene dissolves in benzene but not in water. In the process by which an ionic solid of the type of NaCl enters into solution in water, the molecules of water, because of their high dipole moments, align their negative pole towards the positive ions (Na^+) and the positive pole of H_2O towards the negative ions (Cl^-) at the surface of the crystal. The dipole forces exerted by the oriented water molecules render the inter– ionic attraction within the crystal much weaker than before and some of the ions are thereby pulled away into solution. Assuming that six water molecules are attached to each ion, the schematic representation of the phenomenon of solubility of ionic compounds may be represented as in Fig. 2—3.

The Covalent Bond

Lewis Theory : Atoms may combine with each other chemically by sharing of electrons. A chemical bond of this type is called a covalent bond, and compounds containing these bonds are called covalent compounds. This type of chemical bond was first suggested by G. N. Lewis in 1916.

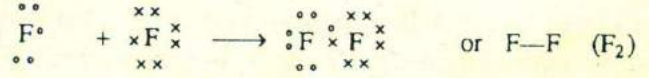
Atoms of different elements or atoms of same element may enter into combination by sharing of electrons to form covalent bond. It may be noted that when the atoms of the same element combine by covalent bond, molecules of the element are formed. When atoms of different elements are covalently bonded, they give rise to molecules of compounds.

Sharing of electrons between atoms always occurs in pairs, and in each pair of shared electrons one is contributed by each atom. Covalent bonds are, therefore, also known as electron pair bonds. One pair of electrons corresponds to a single bond, two pairs to double bond, three pairs of shared electrons to triple bond.

For example, when two hydrogen atoms combine to form a hydrogen molecule, the two hydrogen atoms contribute its single electron to form a pair of electrons shared by both. The resulting electronic arrangement of each hydrogen atom thereby attains the stable electronic arrangement of helium, He(2). The shared electron pair constitutes the covalent bond between the two atoms. The $1s^1$ electron of hydrogen atoms becomes paired up and may be simply represented as,

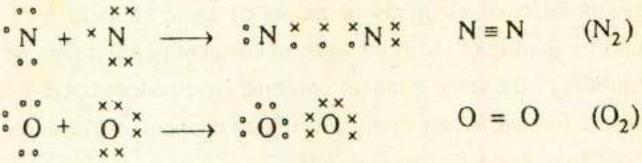
$$H^{\circ} + {\times}H \longrightarrow H : H \quad \text{or} \quad H{-}H \quad (H_2)$$

Similarly, fluorine molecule is formed by combination of two fluorine atoms. Fluorine atom having electron arrangement of $1s^2\ 2s^2\ 2p^5$ has one electron less than the neon atom, $1s^2\ 2s^2\ 2p^6$. Hence if two fluorine atoms combine, one electron from each paired up atoms is shared in common by both the atoms to produce the stable electronic arrangement of neon for the two fluorine atoms.

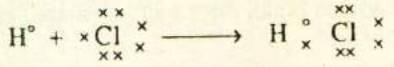


or F—F (F_2)

In both the above examples of the formation of H_2 and F_2 molecules, only one pair of electrons are shared. However, the formation of oxygen and nitrogen molecules by the electron pair bonds can be represented with the help of two pairs and three pairs of electrons respectively. The underlying principle, as discussed before, is the attainment of the stable electronic configurations of the inert gas. Thus,

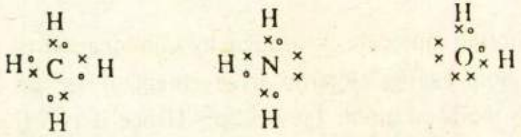


The covalent bond may also link together atoms of different elements to form a molecule of a compound. The combination of a hydrogen atom with an atom of chlorine to form a molecule of HCl may be shown as follows :

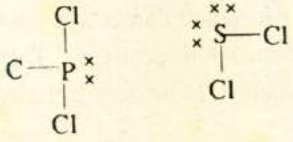


In the molecule of HCl, both H and Cl are surrounded by an electron cloud like that of helium and argon atoms respectively.

An atom can combine by sharing electrons with more than one atom. For instance, in the case of methane, CH_4, ammonia, NH_3, and H_2O, carbon, nitrogen and oxygen have combined with 4, 3 and 2 atoms of hydrogen respectively as illustrated below :



Each of the atoms in CH_4, NH_3 and H_2O has a stable electronic arrangement similar to that of an inert gas. It may be noticed that in NH_3 molecule, there is one pair of electrons which are not shared. These are of special significance and will be discussed latter. Similarly, in the molecule of PCl_3 and SCl_2 each atom contributes an unpaired electron to form an electron pair shared by the two atoms indicated by lines —. Thus,

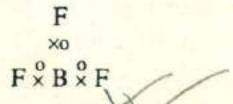


The electronic formula of carbon compounds are easily represented in terms of the formation of covalent bonds.

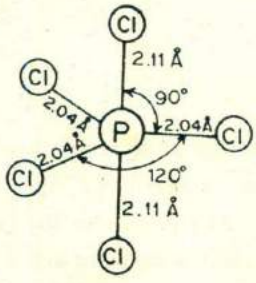
Limitations of Lewis Concept of Covalent Bond

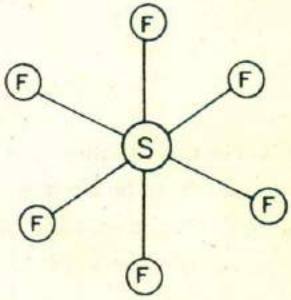
1. The Lewis theory of covalency stressed tendency of reacting atoms to attain the electronic arrangement of inert gas. It, however, did not offer any reason why such a structure was stable. Also no explanation was available why a shared pair of electrons constituted a stable chemical bond. This theory did not present any real understanding of the nature of chemical bond.

2. There are a few molecules in which one of the atoms has not completed the required number of eight electrons. Thus in the case of BF_3, the boron atom has the electron configuration $1s^2\ 2s^2\ 2p^1$. It may be expected that boron would give up its three outermost electrons to give B^{+3}; but these electrons are tightly held. Instead boron shares three electrons with other atoms, say F, to form covalent BF_3. But boron atom does not conform to the stable configuration since it has only 6 electrons in BF_3.



3. Similarly, electronic arrangements for molecules such as PCl_5, ICl_5, SF_6 do not correspond with the Lewis theory and apparently sharing of electrons in pairs involves more than 8 electrons (10 in PCl_5 and 12 in SF_6). Each line represents two electron bonds.





4. Lewis structure of oxygen atom does not explain the magnetic properties of oxygen molecule.

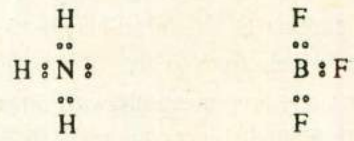
5. There are a large number of compounds where more than one Lewis structures can be shown, although only one compound exists, for example, N_2O, HN_3, CO_2 etc.

Coordination Bond

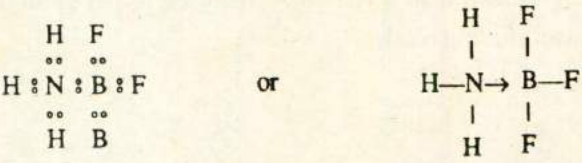
Langmuir Theory : In some molecules one of the atoms may supply both electrons, i. e., both the shared electrons come from the same atom. A covalent bond formed by the donation of a pair of electrons from one atom to another atom in the molecule is called a *coordination bond.*

The electron-dot formula of ammonia and boron trifluoride molecules are represented as,

Ex.



A pair of electron in NH_3 is available for further interaction. A pair of electron of this sort is known as "lone pair" . Since there are only 6 electrons around the boron atom in BF_3, it requires 2 electrons to attain the inert gas configuration. It is known experimentally that gaseous ammonia and gaseous boron triflouride react together to give solid compound $NH_3{:}BF_3$. This can be understood if nitrogen atom shares its lone pair of electrons with the boron atom.



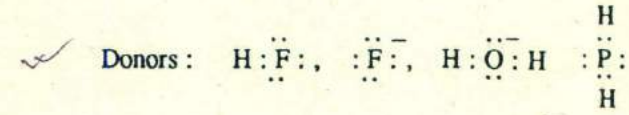
Donor-Acceptor Atoms : In the above case since nitrogen atom supplies or donates both the electrons to form a coordination bond, it is known as donor atom. The atom that accepts the lone pair of electron is known as acceptor atom. The bond between the donor and the acceptor atoms constitutes the coordination bond.

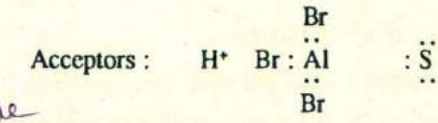
Coordination bonds occur very often in chemical compounds. As mentioned before, two conditions are necessary for the formation of this type of bond :-

(i) One atom, molecule or ion must have an electron pair available for sharing with other atom by donation.

(ii) One atom, molecule or ion must be capable of sharing the lone pair of electrons by acceptance.

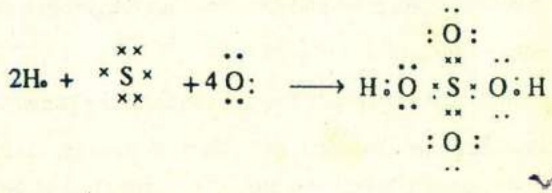
Electronic configurations of some donor and acceptor molecule are given below :-



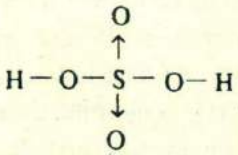


For example

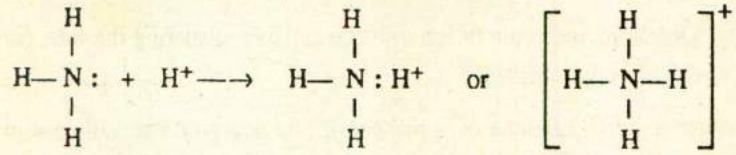
Coordination bonds are particularly important in compounds containing oxygen. For example, a molecule of H_2SO_4 containing 2 H, 1S and 4 O have both covalent and coordinate bonds. The formulation may be represented as,



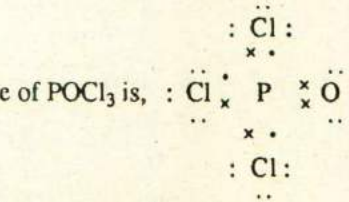
Notice that there are covalent bond between oxygen and hydrogen, covalent bond between sulphur and two oxygen atoms which are joined with the two hydrogen, and two coordination bonds between sulphur and the other two oxygen atoms. This is also represented as :



Ammonium ion also can be represented as formed by the combination of H^+ ion with ammonia molecule by coordination bond.



The electronic structure of $POCl_3$ is,



Recent Theories of Covalent Bonding

It can be easily visualized that when one hydrogen atom with its proton and electron combines with another hydrogen atom with a similar system of proton and electron, there are both forces of attraction and repulsion acting between them. The forces may be classified as :

(a) Repulsion between electron and electron.

(b) Attraction between electrons and protons of each hydrogen atom.

(c) Repulsion between proton and proton.

(d) Electronic interactions between the two electronic systems.

It is necessary here to illustrate the potential energy diagram for the formation of a chemical bond when two atomic systems such as those of two H atoms having their own charge clouds of electrons approach each other. When the two atoms are at infinite distance apart, there is no interaction between their electron clouds. As they approach each other and if there is no chemical bond formation, the energy required to force the two atoms to come close to each other will be very high as indicated by the curve I in Fig 2—4. This shows increasing external energy to force them nearer to each other. On the other hand, the formation of chemical bond between the two atomic systems through electronic interaction leads to the rearrangement of the electron clouds giving rise to the lowering of energy as shown by the curve II in Fig 2—4. The two atomic

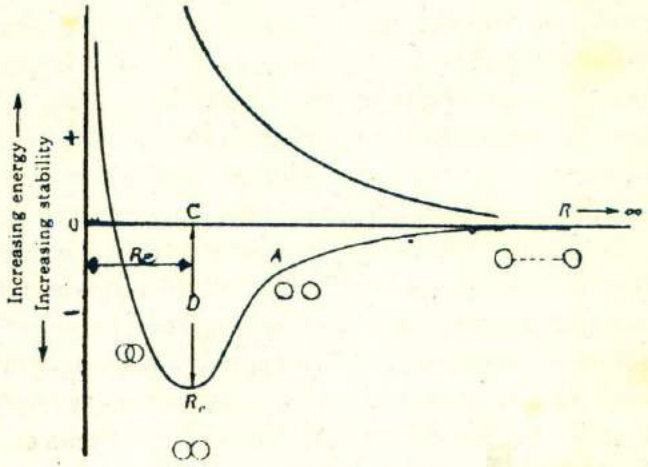


Fig. 2—4. Potential energy diagram for the formation of a diatomic molecule as a function of internuclear distance. Re = Internuclear distance at equilibrium on bond formation. D = Bond dissociation energy.

systems form a molecule with increased stability at the equilibrium internuclear distance between the two atoms. The lowering of energy occurs in chemical bond formation because of the rearrangement of electron clouds of the two systems. The formation of a stable molecule through initially excited states also involves lowering of energy as indicated by Fig. 2—5.

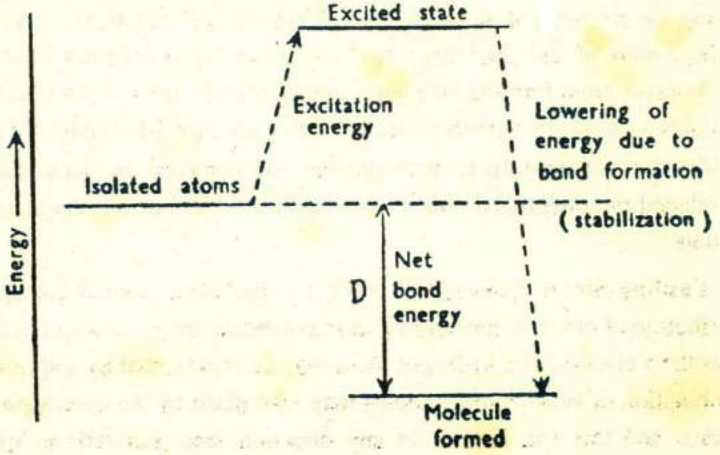


Fig. 2—5. Energy changes during the formation of bond.

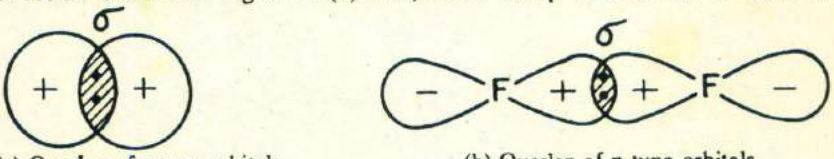
Thus in the case of H_2, theoretical treatment predicts a cloud of two electrons with paired spins between two nuclei. In other cases also the treatment deals with the question of solutions as to how the clouds of valence electrons interact as the atoms are brought together. The treatment is highly mathematical and is beyond the scope of this elementary text book. The entire picture is based upon the wave mechanical approach considering the wave nature of electrons. Briefly it may be mentioned that two main methods have been developed in the application of wave mechanics to the electrons involved in chemical bonding. One of these advanced by Heitler and London in 1927 and extended by Pauling and Slater in 1931, accounts for the directional properties of covalent bond and is known as "valence-bond method". The other method was developed by Hund and Mulliken and postulates the formation of molecular orbitals by superimposition of atomic orbitals to form covalent bond. This method is known as "molecular orbital method".

The Valence-Bond Theory (VBT)

Heitler-London Theory : The Heitler-London concept of covalent bond is based upon the pairing of electrons and resultant neutralization of opposed spins. If the electron spins are opposed when two atoms such as that of hydrogen approach each other, attractive forces result on account of the availability of each orbital in the hydrogen atom for occupation by two electrons without violation of Pauli Exclusion Principle. An atom combines with another atom through the pairing of electrons of opposed spins. Thus nitrogen having the outer electron configuration of $2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$ can share three unpaired electrons with, say, fluorine atom forming NF_3 but cannot form NF_5 since no more orbitals are available in $n = 2$. Phosphorus does form PF_5 because **3d** orbitals are available besides the unpaired **3p** to accommodate the unpaired **3s** electrons. Pauling introduced the directional characteristics on the basis of the shapes of atomic orbitals.

Pauling-Slater Concept of VBT : It has been pointed out before that distribution of electron densities in various orbitals are geometrical in character. Thus the s electron of a hydrogen atom may be represented by a sphere and the combination of two hydrogen atoms may take place by the overlapping of two spheres and this can happen in any direction since s orbitals are spherically

symmetrical as shown in Fig. 2—6 (a). The overlap of two **p** orbitals in x direction is shown in Fig. 2—6 (b). But, since the p orbitals are directed in



(a) Overlap of s-type orbitals (b) Overlap of p-type orbitals

Fig. 2—6. Overlap of **s** and **p** orbitals. Notice the + and − signs which must have the same sign for combination of orbitals.

space along x, y and z axes, and are at right angles to each other, it follows that bonds involving these orbitals must be similarly directed. Pauling and Slater put forward the concept of directed bond based upon the consideration that strong covalent bonds are formed by maximum overlapping of atomic orbitals which gives the resultant maximum electron densities in the bond regions. However, there are certain conditions for the combination of atomic orbitals which may be stated, in short, as follows :

1. The orbitals must have similar energies.
2. The orbitals must overlap to a considerable extent.
3. The orbitals must possess the same symmetry about the molecular axis.
4. According to Pauli Exclusion Principle, each bonding orbital contains two electrons of opposed spin.

Thus **s** orbitals can combine with another **s** or **p** or **d** orbitals in the direction of the bond. A p_x orbital can combine with another p_x orbital but not with p_y orbital in the same system. If two p_y orbitals combine they do so sideways or laterally. These are illustrated in Fig. 2—7.

In the case of water, oxygen atom with $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$ electron configuration containing two unpaired electrons combine with two **s** electrons of opposite spins of two hydrogen atoms to form H_2O. But P_y and P_z orbitals are at right angles to each other; the two O—H bonds in H_2O are expected to be at right angles (90°) as shown in Fig. 2—8. In practice the bond angles in H—O—H has been found to be about 105° instead of 90°. This has been assumed to be due to repulsion between the charged clouds of two H atoms. Similar is the case in H_2S but the bond angle is 92° in this molecule. The larger angles than 90° in H_2O have been assumed to be due to the formation of *hybrid* bonds by O rather than simple overlap of **s** and **p** orbitals.

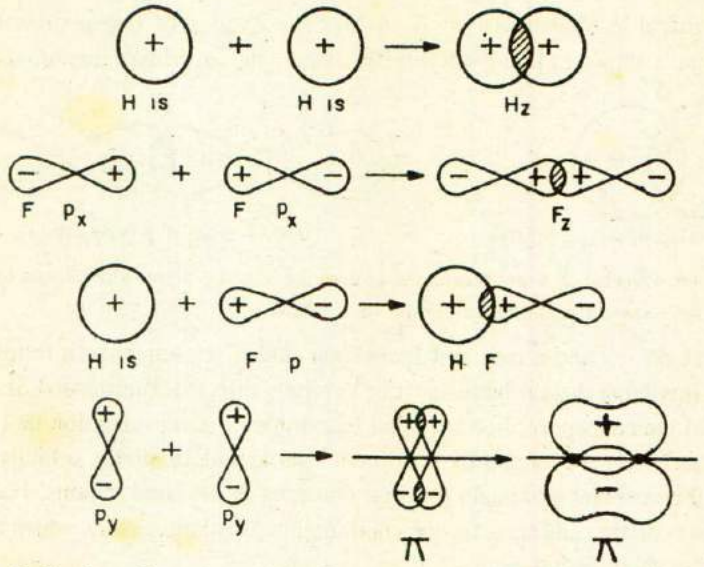
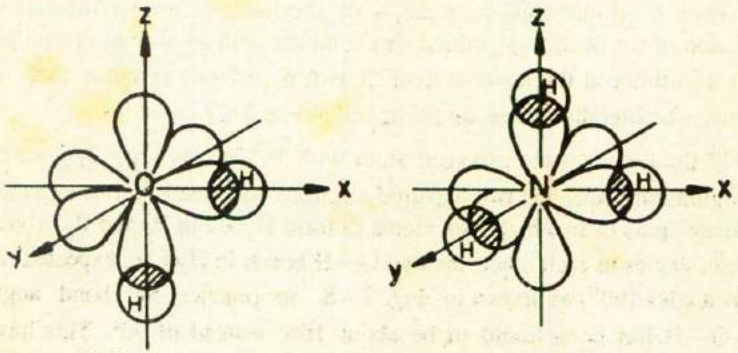


Fig. 2—7. Overlap of atomic orbitals. The signs (+ or −) of the combining orbitals must be the same. No overlap takes place when the orbitals are of opposite sings.

Nitrogen has three p electrons occupying singly the p_x, p_y and p_z orbitals. These combine with the s orbitals of three hydrogen atoms in a similar manner forming NH_3 having the three bonds at right angles (Fig. 2—8) to each other. In



H_2O NH_3

H—O—H angle 90° Each H — N—H angle 90°

Fig. 2—8. Overlap of orbitals in H_2O and NH_3 molecules without the use of hybrid orbitals gives wrong structures.

practice the angles between H—N—H in NH_3 has been found to be about 107°. This has been suggested as due to the repulsion of the hydrogen atoms. But this is now explained on the basis of hybrid bonds in which N uses four hybrid tetrahedral orbitals rather than simple orbitals. Similar is the case of O in H_2O.

Hybrid Bonds

The bonds in simple molecules such as $BeCl_2$, BF_3, CCl_4, H_2O, NH_3, PCl_3, PCl_5 etc. can be best explained on the basis of valence bond theory in terms of the formation of hybrid bond orbitals by the central atoms in the molecules. Beryllium having $1s^2\ 2s^2$ in the ground state has paired electrons. Similarly, B with $1s^2\ 2s^2\ 2p^1$ appears to be monovalent and C with $1s^2\ 2s^2\ 2p^2$ or $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$ should be at best a divalent atom. But these atoms use different hybrid bonds.

sp Hybrid Bonds :

In $BeCl_2$, the two bonds Be—Cl are linear and equivalent in all respects. Similarly in BF_3, CCl_4 etc. the bonds are equivalent and the molecules have definite geometry. The ground state and the excited state of the electron configurations in the atoms of Be, B, C are expressed as

Be—$1s^2\ 2s^2$	excited	$1s^2\ 2s^1\ 2p_x^1$
B—$1s^2\ 2s^2\ 2p_x^1$	excited	$1s^2\ 2s^1\ 2p_x^1\ 2p_y^1$
C—$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$	excited	$1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$

The two bonds of Be in $BeCl_2$ are not formed separately by the overlap of Be $2s^1$ with one Cl p_x^1 and then Be $2p_x^1$ with another Cl p_x^1 since in this way Cl—Be—Cl would not have been linear. It is, therefore, concluded that Be $2s^1$ and $2p_x^1$ orbitals combine to form two sp hybrid orbitals at 180° to each other. The bonds in $BeCl_2$ are formed by the overlap of p_x orbitals of two Cl atoms with the hybrid sp orbitals of Be atom as given in Fig. 2—9.

sp^2 Hybrid Bonds

Similarly, B atom in BF_3 does not use $2s^1$, $2p_x^1$ and $2p_y^1$ orbitals separately to form bonds with three F atoms, but a combination of $2s^1$, $2p_x^1$ and $2p_y^1$ orbitals giving rise to hybrid sp^2 bond orbitals situated in space at the

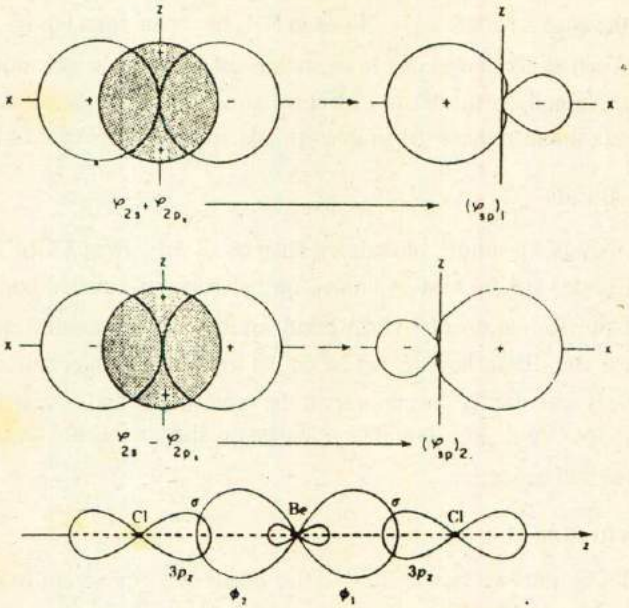


Fig. 2—9. Formation of sp hybrid orbital by combination of separate s and p orbitals. Overlap of p orbitals of two Cl atoms with sp hybrid orbital of Be forming σ bonds.

corners of an equilateral triangle giving each F—B—F angle equal to 120°. This is illustrated in Fig 2—10.

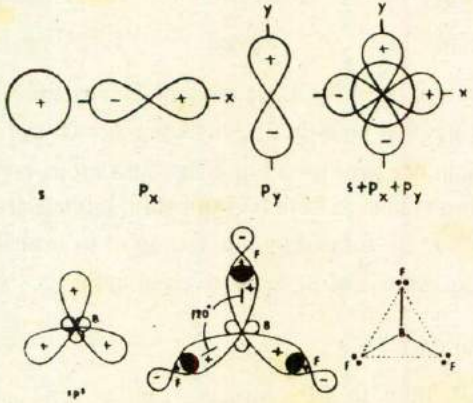


Fig. 2—10. Formation of sp^2 hybrid orbitals of B from one s and two p orbitals. Formation of BF_3 molecule .

sp^3 Hybrid Bonds :

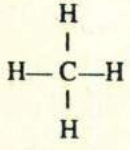
The electronic configuration of an isolated carbon atom is $1s^2\ 2s^2\ 2p^2$. In terms of the orbital theory there are three p orbitals, each of which initially contains one electron because of the same energy before pairing occurs. The detailed configuration of carbon atom may be writtern as $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^\circ$. The vacant p orbital is written as p_z°. Thus the valence electrons of carbon in the ground state are—

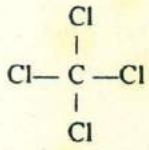
$$2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$$

Since carbon forms four covalent bonds, the above arrangement of the valence electrons does not explain this nature of the carbon atom. It only indicates that carbon can form only two covalent bonds. It is, therefore, considered that an excited state of carbon atom is attained by promoting one of the $2s^2$ electrons to the vacant $2p_z^0$ orbital. The excited state of the carbon has the electronic arrangement of the valence shell as,

$$2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$$

Thus the carbon atom can now form four covalent bonds by sharing 4 electrons from another atom or atoms with one electron of 2s and three electrons of 2p orbitals. One may expect that carbon atom will, therefore, form one bond of one kind and three bonds of another kind. But the four bonds of carbon are equivalent in all respects and there is no difference in the four bonds of either CH_4 or CCl_4.





Actually, the one 2s orbital and the three 2p orbitals of carbon atom combine to form four hybrid orbitals which are now completely equivalent to one another. These four hybrid orbitals are directed in space at the corners of a regular tetrahedron.

$$s + p_x + p_y + p_z = sp^3 \text{ hybrid orbitals.}$$

These hybrid orbitals of C form four bonds with 1s orbital of 4 H atoms or p_x orbital of 4 Cl atoms in CH_4 and CCl_4 respectively.

These four hybrid bonds are stronger than either **s** or **p** bond orbitals when formed separately. This is the reason that four bonds of carbon are tetrahedral having bond angles of 109°28′ (Fig. 2—11).

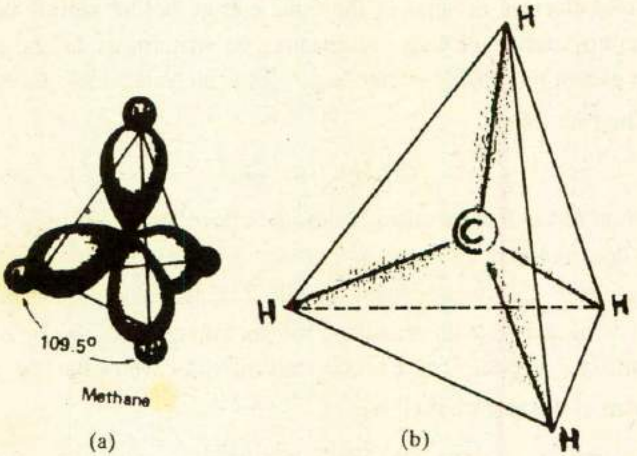


Fig. 2—11. (a) Tetrahedral sp^3 bond of carbon as in CH_4. (b) Overlap of sp^3 hybrid orbitals of C with **s** orbitals of H. The four C—H bonds are shown by the solid lines in (b).

Similarly, other types of hybrid bonds are formed having directional characteristics by combination of different atomic orbitals. Some of them are designated as **sp**, sp^2, dsp^2, sp^3, sp^3d, d^2sp^3 etc. which have linear, triangular, planar, tetrahedral, trigonal bipyramidal and octahedral arrangements respectively.

Hybrid orbitals	*Geometry of molecules*	*Examples*
sp	Linear	$BeCl_2$, $HgCl_2$
sp^2	Triangular	BBr_3, BF_3
sp^3	Tetrahedral	CH_4, $SiCl_4$
dsp^2 or sp^2d	Square planar	$Ni(CN)_4^{-2}$, XeF_4
sp^3d or dsp^3	Trigonal bipyramidal	PCl_5
d^2sp^3, or sp^3d^2	Octahedral	SF_6, $Co(NH_3)_6^{+3}$

Other forms of hybrid orbitals have been described in appropriate places.

We notice that the geometry of a specific molecule is described by converting atomic orbitals into *HYBRID ATOMIC ORBITALS* (These are formed by

mathematical combination of two or more pure atomic orbitals). Thus a hybrid orbital is different from a pure orbital in contour and directions in space. A tetrahedral hybrid atomic orbitals are each described as having $\frac{1}{4}$ s and $\frac{3}{4}$ p atomic orbital character. A trigonal plane hybrid orbital has $\frac{1}{3}$ s and $\frac{2}{3}$ p character. The linear hybrid orbital is constituted by combination of $\frac{1}{2}$ s and $\frac{1}{2}$ p character.

The Bonding operation, thus in the case of hybrid orbitals are due to overlapping of the hybrid orbitals with pure or another hybrid orbitals according to Linear Combination of Atomic Orbitals (LCAO). Since the hybrid orbitals have equal bond length, bond energy and bond strength, these are also known as equivalent orbitals.

Diagramatically the energetics involved in the formation of some hybrid orbitals are shown in Fig. 2—12 to Fig 2—22.

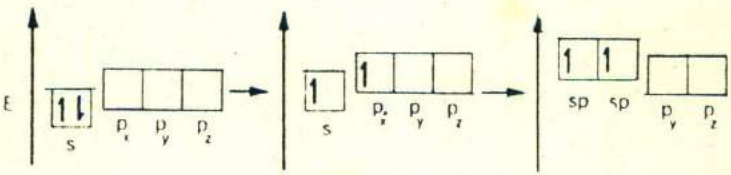


Fig 2—12, Energy diagramme for the formation of sp hybrid atomic orbitals.

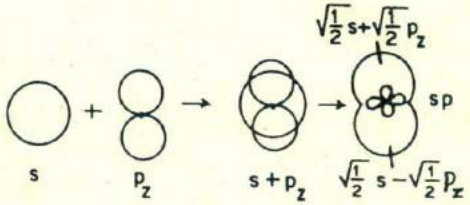


Fig 2—13, Mathematical combination of two sp hybrid orbitals

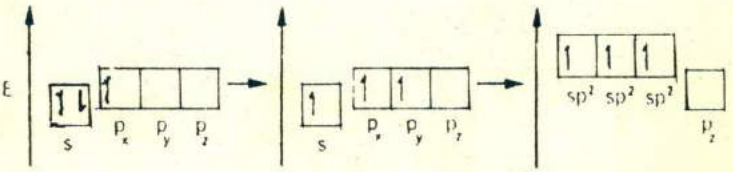


Fig 2—14, Energy diagramme of sp^2 hybrid orbital.

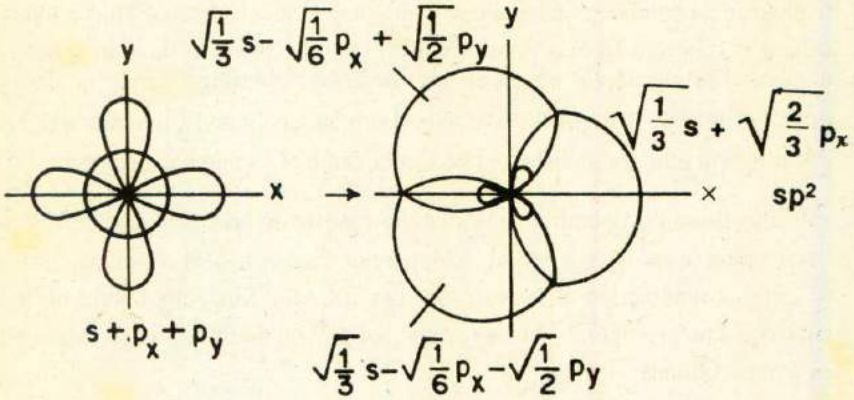


Fig 2—15, Combination of $s + p_x + p_y$ orbitals to give sp^2 hybrid orbitals and their orientations.

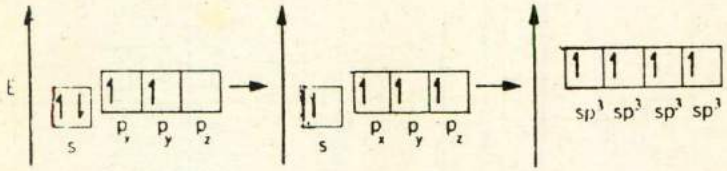


Fig. 2—16 Sequence of Energy Diagrams representing the formation of sp^3 Hybrid Atomic Orbitals from Pure Atomic Orbitals

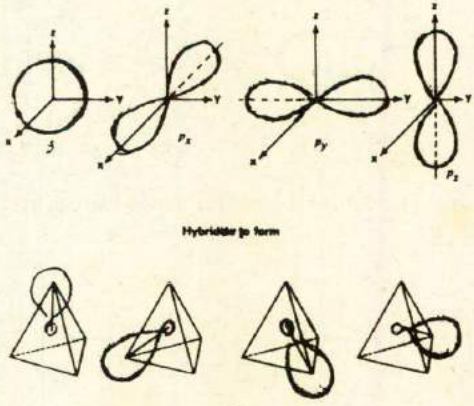


Fig. 2—17 A Tetrahedral Assemblage of Four sp^3 Hybrid Atomic Orbitals

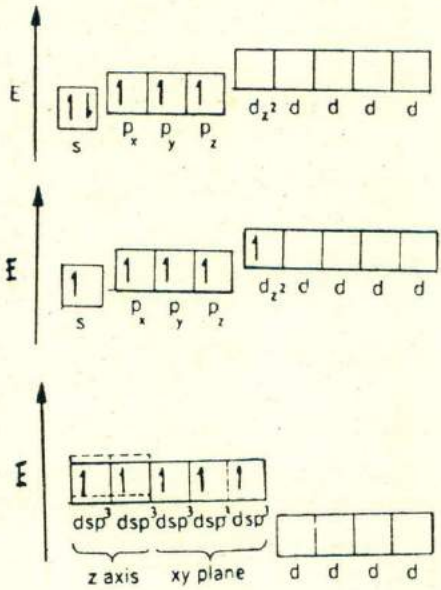


Fig. 2—18 Sequence of Energy Diagrams representing the formation of dsp^3 Hybrid Atomic Orbitals from Pure Atomic Orbitals

$$s + p_x + p_y + p_z + d_{z^2}$$

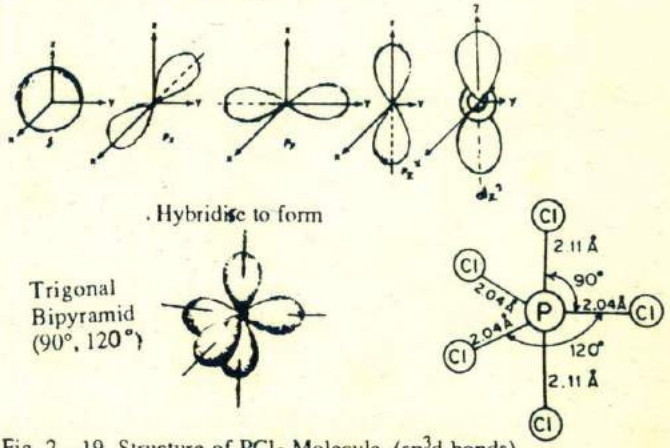


Fig. 2—19. Structure of PCl_5 Molecule. (sp^3d bonds)

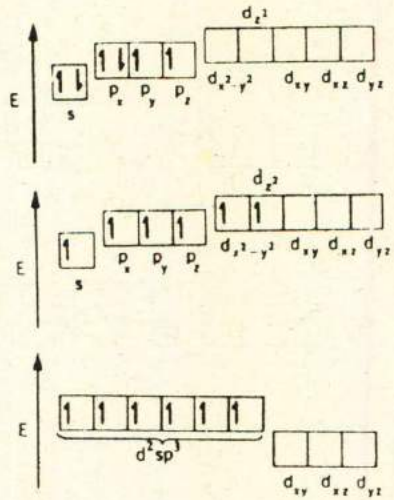


Fig. 2—20. Sequence of Energy Diagrams representing the formation of d^2sp^3 Hybrid Atomic Orbitals from Pure Atomic Orbitals in a Sulphur Atom

$$s + p_x + p_y + p_z + d_{x^2-y^2} + d_{z^2}$$

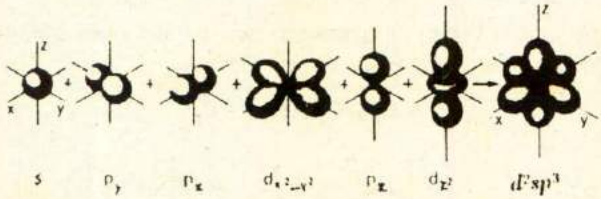


Fig. 2—21. Pictorial Representation of the Mathematical Interpretation of the formation of Six d^2sp^3 Hybrid Atomic Orbitals

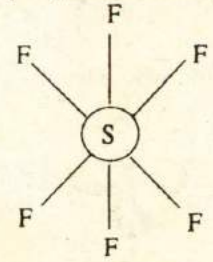
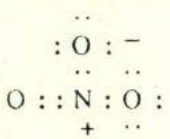


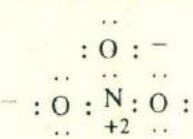
Fig. 2—22. Pictorial representation of the Mathematical Interpretation of the formation of a Molecule of SF_6 using sp^3d^2 hybrid orbitals of S

Resonance

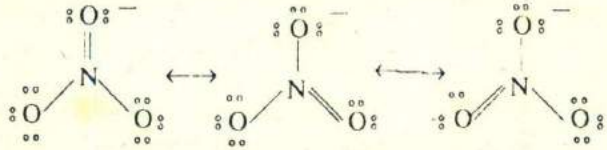
NO_3^-, CO_3^{-2}, SO_3^{-2}, O_3 etc indicate different electron distributions in their respective molecular species according to Lewis method. For instance in the Nitrate (NO^{-3}) ion, the N—O bond lengths are the same and all the O—N—O angles are equal to 120°. NO^{-3} may be shown to have electron distribution as :



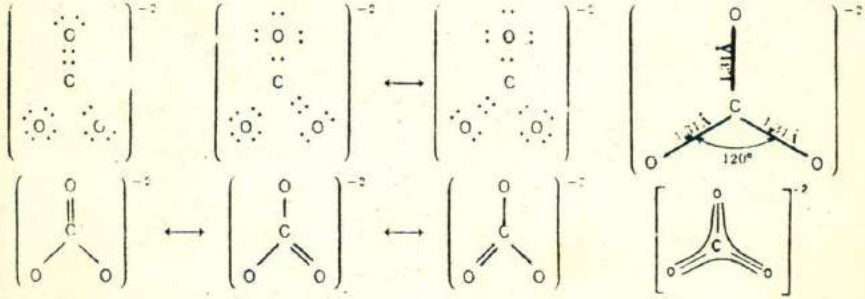
But the experiment shows that NO_3^- must have electron distribution as :



But the charge separation is too great to accept this electron distribution. Thus the nature of bonding in NO^{-3} CO_3^{-2}, etc. may be represented by several different structure having different positions of the double bonds as :



Such molecules or ions may be considered to have resonance structures having different positions of the electrons and do not have a single formula. In this case it may be assumed that each bond between N—O is formed by $1\frac{1}{3}$



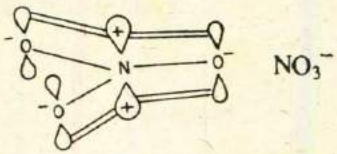
electron pairs. The chemical structures in which the bond orders are not integers (whole numbers) are called hybrid structures or resonating structures. The resonance characteristics demands that the molecular models have a series of bond symbols as in the case of CO_3^{-2}

Rules for Resonance

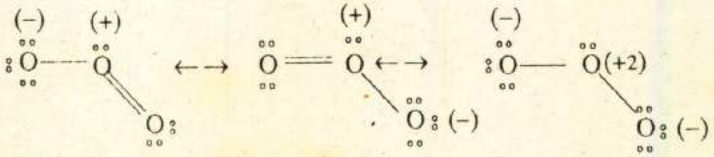
The following rules have been formulated for the resonance structures :

1. A resonance hybrid structure of a chemical species must have two or more conventional bond symbols.
2. The relative positions of the component atoms must be fixed in the various forms having similar electron arrangements.
3. Each conventional structural formula of a hybrid molecule must have the same number of unpaired electrons.
4. The different resonance hybrid must have similar energy and the resultant structure must be of lower energy for the species to be stable.
5. The change in the electron positions between the hybrid structures is made in the π– bonding system.
6. The maximum effect of resonance appear in planar chemical structures because of π– bondings.
7. Unlike charges in the stable molecular structures are least separated and like charges are greatly dispersed.
8. The greater the number of contributing structures, the more stable is the hybrid molecule or species.

Considering the NO_3^- ion in the orbital forms in which N—O bonds have the same character, the resulting picture shows three p_z orbitals of each oxygen having two electrons, N has a vacant p_z orbital giving π- bonding.



O_3 molecule may be represented as :



Types of π– bonded systems having Resonance Structures

1. Diatomic hybrid molecules: CO and NO

$$:\overset{\cdot\cdot}{N}::\overset{+}{\underset{\cdot\cdot}{O}}: \leftrightarrow :\overset{\circ}{N}:::\overset{+}{O}: \leftrightarrow :N:::\overset{\circ}{O}: \leftrightarrow :\overset{\circ}{N}::\overset{\cdot\cdot}{O}:$$

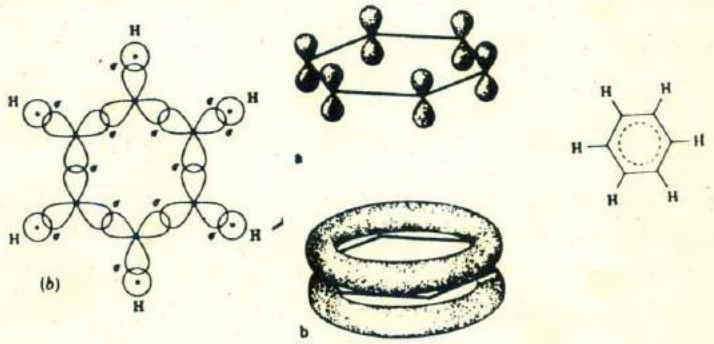
$$\leftrightarrow :\overset{\circ}{N}:\overset{+}{\underset{\cdot\cdot}{O}}:$$

$$:C\equiv\overset{+}{O}: \leftrightarrow :C=\overset{\cdot\cdot}{O} \leftrightarrow :\overset{+}{C}-\overset{\cdot\cdot}{O}:$$

2. Triatomic hybrid molecules such as CO_2 may be represented as:

$$:\overset{+}{O}\equiv C-\overset{\cdot\cdot}{O}: \leftrightarrow \overset{\cdot\cdot}{O}=C=\overset{\cdot\cdot}{O} \leftrightarrow :\overset{\cdot\cdot}{O}-C\equiv\overset{+}{O}:$$

3. Tetratomic molecules having conjugated double bonds as in butadiene $H_2C = CH—CH = CH_2$.
4. Hexagonal planar structure of benzene is one of the historical example of the resonance structure showing several hybrid structures having double delocalized π- electron clouds on top and the bottom of the 6C—C ring systems as shown belows :



Wave mechanical representation of a benzene molecule (*a*) represents p_z atomic orbital overlap of *C* to form continuous π-electron cloud above and below the plane of C nuclei. (*b*) represents the three-dimensional wave clouds.

Experimental Evidence of Resonance : 1. Shortening of bond length measured by x-ray diffraction, 2. Benzene does not give reactions of isolated double bonds, 3. Infrared frequency indicate resonance, 4. Measured heat of formation differ from the calculated value, 5. Dipole moment measurements indicate resonance.

The Molecular Orbital Theory (MOT)

According to the molecular orbital theory of chemical bond, each electron is placed in a molecular orbital which is polynuclear, that is, it is associated with all the atomic nuclei present in the molecule. the electrons are placed into the available molecular orbitals one at a time, the lowest energy molecular orbital being filled first. In terms of Pauli Exclusion Principle each molecular orbital can accommodate a maximum of two electrons provided their spins are opposed.

The fundamental principles involved in the molecular orbital theory for the combination of atomic orbitals are the same as those of the Valence Bond Theory, namely,

(i) The orbitals must have similar energy;

(ii) The orbitals must overlap to a considerable extent ;

(iii) The orbitals must have the same symmetry about the molecular axis.

The mathematical treatment for the combination of atomic orbitals in order to obtain the molecular orbitals is known as the Linear Combination of Atomic Orbitals or in short LCAO approximation method. The linear combination of two atomic orbital wave functions, ψ_A and ψ_B,combine to form two new molecular wave functions expressed by equations,

$$\psi_+ = C_A\psi_A + C_B\psi_B \qquad \psi_+^2 = C_A^2\psi_A^2 + 2C_A\psi_A C_B\psi_B + C_B^2\psi_B^2$$

$$\psi_- = C_A\psi_A - C_B\psi_B \qquad \psi_-^2 = C_A^2\psi_A^2 - 2C_A\psi_A C_B\psi_B + C_B^2\psi_B^2$$

ψ_+ and ψ_- are the molecular orbital wave functions and C_A and C_B are the mixing coefficients of atoms A and B respectively. For a homonuclear diatomic molecule A_2 when A = B, the wave functions ψ_A and ψ_B are equal and $C_A^2 + C_B^2 = 1$, i. e., $C_A = C_B$ (mathematical details omitted). Then $C_A^2 = C_B^2 = \frac{1}{2}$ for a homonuclear bond and for a heteronuclear bond (ionic bond) $C_A^2 = C_B^2 = 1$, $C_A^2 = 0, C_B^2 = 1$

In a purely covalent bond the bonding electron wave is distributed equally between A and B and the limiting condition of a completely ionic bond, the bonding electron wave reside within the valence level of atom B to produce a negative charge atom. A having none of the electron wave in the valence level, has a residual positive charge. Thus $C_A^2 = 0$ and $C_B^2 = 1$.

Thus the combination of two atomic orbitals gives two molecular orbitals (one of higher energy and the other of lower energy) which accommodate the available electrons. Each orbital contains a pair of electrons of opposed spins. The molecular orbitals which are at a lower energy than the original atomic orbitals are known as *bonding molecular orbitals*. The molecular orbitals which are at a higher energy than the original atomic orbitals are known as *antibonding molecular orbitals*. Electrons which are placed in a bonding molecular orbital are known as *bonding electrons* and signify attraction. Electrons which are placed in an anti-bonding molecular orbital are known as *anti-bonding electrons* and signify repulsion. Electrons present in the deep-seated non-bonding orbitals do not take part in bonding and are known as *non-bonding* electrons.

In the formation of a stable molecule, the number of bonding electrons must be more than the number of anti-bonding electrons. These effects are illustrated in Fig. 2—23 showing the formation of hydrogen and helium molecules by the LCAO method. The hydrogen molecule contains two bonding electrons in the lowest energy bonding orbital labelled as 1s. This can be written as,

$H(1s^1) + H(1s^1) = H_2[(\sigma 1s)^2]$. The upper anti-bonding orbital labelled as σ^*1s is empty.

That a molecule of helium gas He_2 is not formed, is easily explained on the basis of the molecular orbital theory as shown in Fig. 2—23. The number of electrons in the bonding σ 1s and antibonding σ^* 1s are equal and hence the attraction and repulsion between the electrons of the two atoms of helium are equal. Thereby helium molecule He_2 is not formed.

Similarly, a nitrogen molecule is formed by the union of two atoms of nitrogen having configuration $1s^2\ 2s^2\ 2p^3$. The $1s^2$ electrons nearest the nucleus are non-bonding and may be omitted for simplicity. The $2s^2$ and $2p^3$ electrons of the two nitrogen atoms take part in bonding interactions. Thus $N(1s^22s^22p^3) + N(1s^22s^22p^3) = N_2[KK\ (\sigma 2s)^2\ (\sigma^*2s)^2\ (\sigma 2p)^2\ (\pi 2p)^4]$. KK symbols indicate K shells containing the non-bonding electrons in the Is levels. Of the four 2s electrons from the two atoms of nitrogen, two become $(\sigma 2s)^2$ bonding electrons and two become $(\sigma^*2s)^2$ which are anti-bonding. The effect of the two molecular

orbitals $\sigma 2s$ and $\sigma^* 2s$ in the N_2 molecule each containing 2 electrons is cancelled out and they do not take part in the bonding system of N_2.

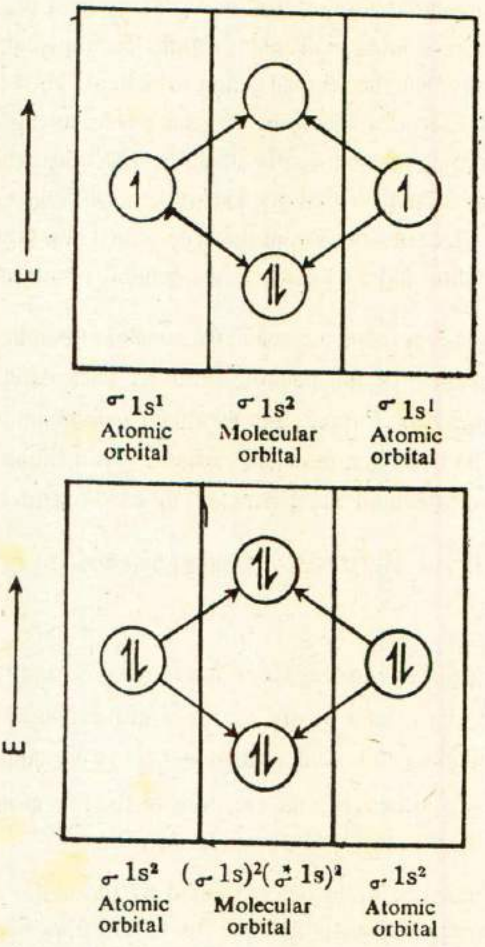


Fig. 2—23. Formation of H_2 molecule (top) and repulsion of He atom (bottom)

The p orbitals of the two nitrogen atom can combine in two different ways. The direct head-on or end-on combination of p orbitals, as in the case of two p_x atomic orbitals, form a bonding molecular orbital known as $\sigma 2p_x$ molecular

orbital and another anti-bonding molecular orbital σ^*2p_x. Another way of combination of p orbitals takes place side-ways or laterally. If two $2p_y$ orbitals are combined side-ways to give two molecular orbitals, the bonding molecular orbital is labelled as $\pi 2p_y$ and the anti-bonding molecular orbital is designated as π^*2p_y. Similarly, the combination of the p_z orbitals gives $\pi 2p_z$ bonding and π^*2p_z anti-bonding molecular orbitals. The six p electrons of the two N atoms consisting of two sets of $2p_x^1$, $2p_y^1$ and $2p_z^1$ atomic orbitals which interact to form two $\sigma 2p_x$ or $(\sigma 2p_x)^2$ and four electrons become $\pi 2p_y^2$, $\pi 2p_z^2$ and all are bonding electrons because of lower energy than in the isolated atoms. The six bonding electrons produce a N ≡ N triple bond, one bond being σ and other two π in character. The formation of nitrogen and oxygen molecules according to molecular orbital treatment is shown in Fig. 2—24.

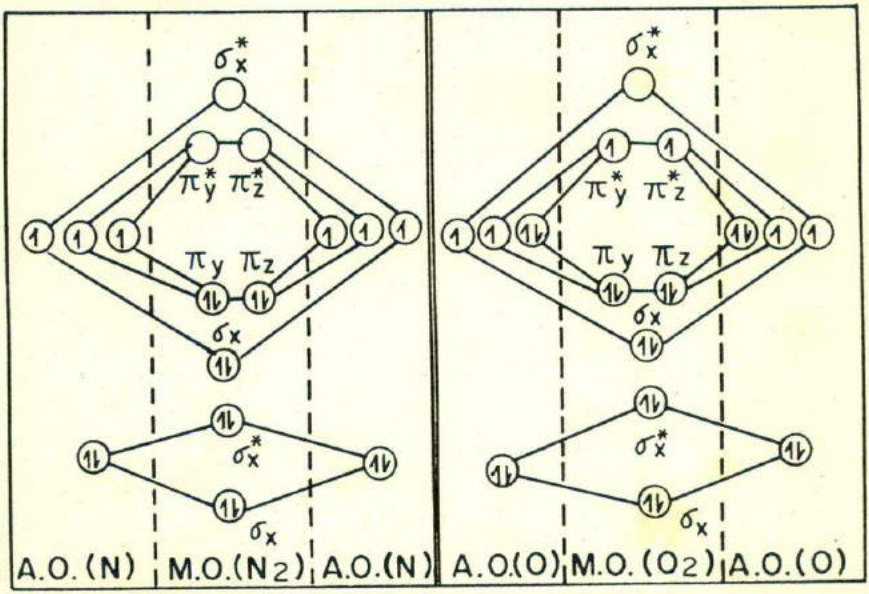


Fig. 2—24 Formation of (N_2). and (O_2) molecular orbitals. Bond order, N_2 = 3 Bondorder for O_2 = 2. Notice 2 unpaired electrons in the O_2 molecule.

Bond Order:

Bond order is defined as equal to half the total number of electrons in the bonding orbitals (Nb) minus half the number of electrons in the anti-bonding orbitals

(Na). That is : Bond order $= \frac{1}{2}$(Nb—Na). For a stable molecule the number of electrons in the bonding orbitals must be greater than the number of electrons in the anti-bonding orbitals. Bond orders in some diatomic homonuclear molecules and the relationship with some important properties are given in Fig. 2—25. The two dimensional overlap of s and p orbitals according to MOT are given in Fig. 2—26.

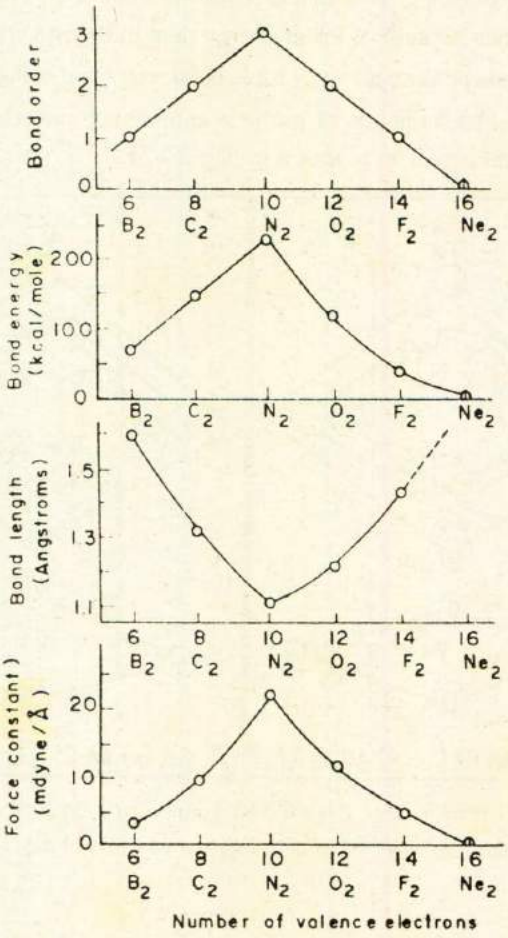


Fig. 2—25. Bond orders and bond properties in some homonuclear diatomic molecules.

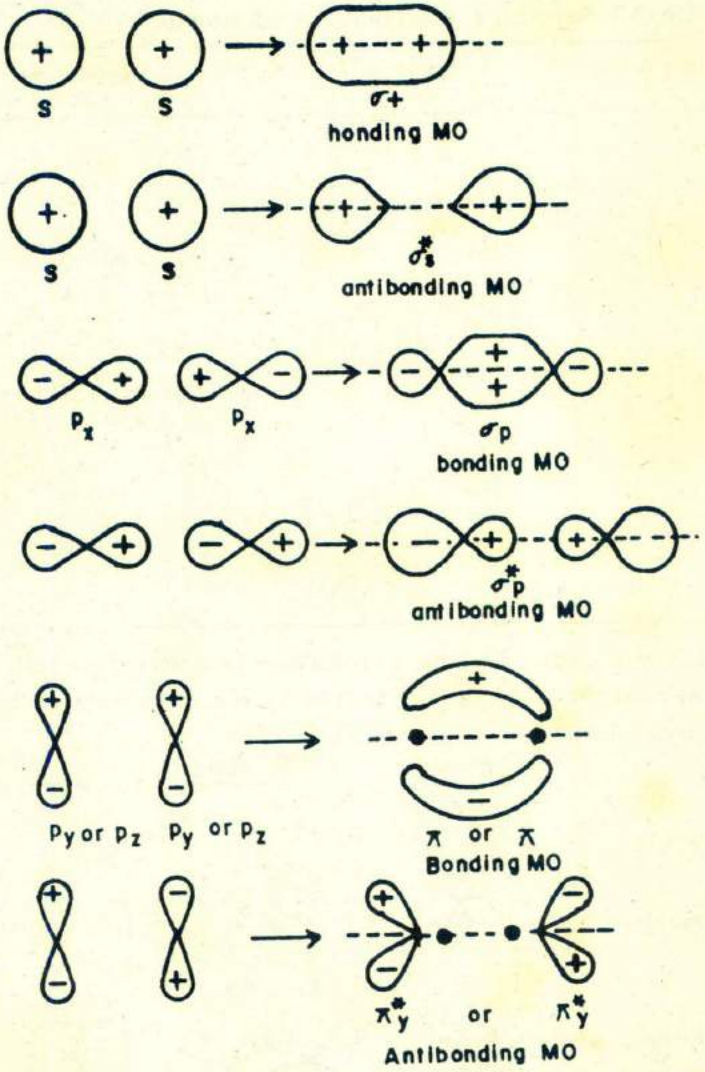


Fig. 2—26 Cross-section of approximate shapes of MO's in homonuclear molecules.

The combinations of atomic orbitals to form molecular orbitals are governed by energy and symmetry consideration and the permitted combinations are given in Table 2.2.

Table 2.2 Permitted combinations of atomic orbitals.

Atomic orbital ψ_A		Atomic orbital ψ_B			Type of molecular orbital formed
s	s	p_x	$d_{x^2-y^2}$	d_{z^2}	σ
p_x	s	p_x	$d_{x^2-y^2}$	d_{z^2}	σ
p_y		p_y	d_{xy}		π
p_z		p_z	d_{xz}		π
$d_{x^2-y^2}$	s	p_x	$d_{x^2-y^2}$	d_{z^2}	σ
d_{z^2}	s	p_x		d_{z^2}	σ
d_{xy}		p_y	d_{xy}		π
d_{xz}		p_z	d_{xz}		π
d_{yz}			d_{yz}		δ
$d_{x^2-y^2}$			$d_{x^2-y^2}$		δ

It is to be noted that σ MO has no nodal plane, a π MO has one nodal plane and a δ MO has two nodal planes. The cross sections of end-view of the three types of molecular orbitals are given in Fig. 2—27.

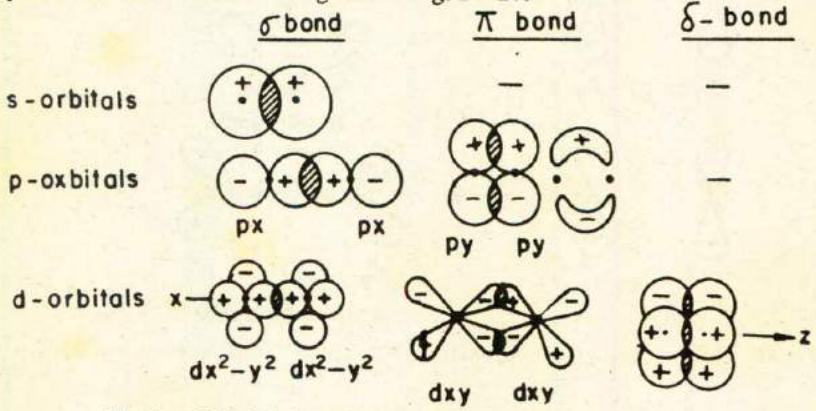


Fig. 2—27 Nodal planes in (a) σ MO, (b) π MO and (c) δ MO.

It may be noted that both the valence bond theory and molecular orbital theory distinguish σ and π types of bonds.

σ and π Bonds:

As a result of the difference in the symmetry of electron distribution, two different kinds of bonds may also be distinguished. In the single bonds, direct or head-on overlap of atomic orbitals produces electron density symmetrical to the bond direction in the molecule. This type of bond is called a *sigma bond* (σ bond). Almost all single bonds have the maximum electron densities between two atoms and are, therefore, σ bond.

The lateral or sideways overlap of orbitals produces an electron cloud having the plane of symmetry in the bond direction and lying above and below the molecular axis. Such bonds are known as *pi-bonds* (π bond).

The head-on overlap of **s** orbitals of hydrogen with that of **p** orbitals of oxygen in H_2O produces two σ bonds in H σ O σ H. (Fig. 2—8 page 76).

Similarly, three σ bonds are formed in NH_3 molecules between N and H as shown in Fig. 2—8.

In ethylene, however, the hydrogen atoms are bonded by σ bonds and carbon atoms by a σ and a π bond as shown in Fig. 2—28

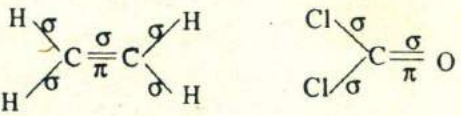


Fig. 2—28. Overlap of p_z orbitals in C_2H_4. The horizontal double lines indicate (C—C) one σ bond and one π bond. The four hydrogen are bonded by 4(C—H) σ bonds. $COCl_2$ also has 2 O—Cl σ bonds, one C—O σ bond and one C—O π bond.

The overlap of π orbitals of two nitrogen atoms to form a molecule of N_2 may be shown as in Fig. 2—29 giving a σ bond and two π bonds.

Some Properties of Covalent Bond

Molecules formed by covalent bonds have come into existence by sharing electron pair or pairs. The total distribution of electricity with each atom is, therefore, unchanged. As each atom remains electrically neutral, the molecule has

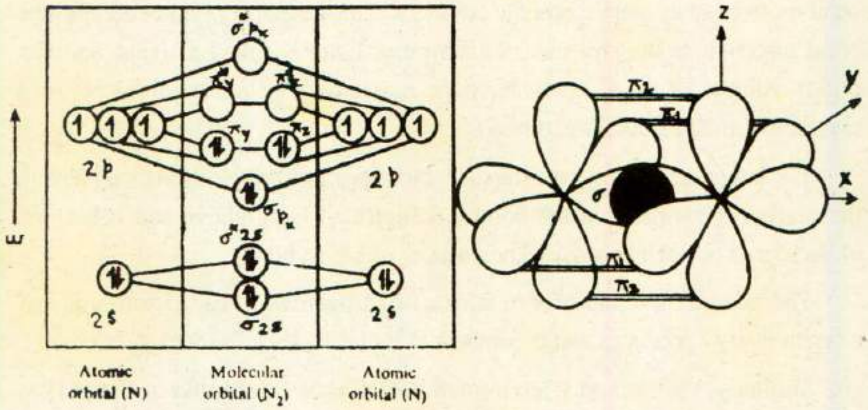


Fig. 2—29 Formation of N_2 molecule. A σ bond is shown by black shading at the centre and the horizontal double lines indicate formation of two π bonds.

no external field of force and covalent compounds are consequently either gases or liquids and solids which have low melting points and are easily vapourized. Covalent bond produces directed bonds and the crystals are made up of atoms held together by definite chemical bonds. Organic compounds provide ample examples.

Covalent compounds do not generally conduct electricity and do not exhibit isomorphism. Due to the factors such as atomic size and electronegativity of the constituent atoms, a covalent compound may tend to be polar in character and shows high dipole moments and dielectric constants. Hence a polar liquid, such as water, is a good ionizing solvent and when associated, it possesses co-ordination characteristics and although shows little tendency to ionize itself, it can dissolve most of the ionic compounds. Water has a dielectric constant of about 80 as compared to about 2 of benzene and paraffins which are non-polar and do not allow dissociation of ionic solids to take place.

Polar molecules have a tendency to exhibit dipole association as mentioned in the case of water. On account of the attractions of opposite poles in a polar

molecule abnormal behaviours are shown in liquids. The more polar the substance the greater is the intermolecular attractions. This point has also been discussed in connection with hydrogen bond. Thus polar compounds have higher melting points and boiling points as compared to non-polar covalent compounds. It has already been mentioned that ionic compounds have very high melting and boiling points due to considerable amount of work which must be done to separate the lattices.

Covalent compounds are usually stable and reactions between covalent molecules usually take place by way of unstable intermediaries. Covalent compounds are normally soluble in non-polar solvents. These are usually sparingly soluble in water. Some covalent compounds dissolve freely in water because they react with it chemically :

$$HCl + H_2O = [H_3O]^+ + Cl^-$$

$$NH_3 + H_2O = [NH_4]^+ + OH^-$$

Ethyl alcohol and sucrose dissolve in water due to hydrogen bonding.

One special feature of covalent bonds is that they are directed in space and their relative positions are almost fixed. It is quite possible to have the same groups arranged round an atom in more than one way. In other words, structural and stereoisomerism are possible among groups whose constituent atoms are held together by covalent linkages. This particular aspect gives rise to stereoisomerism and optical isomerism in organic compounds and also in inorganic complexes.

Distinction between ionic and covalent bonds :

In general, the following points of distinctions may be noted regarding the properties associated with the two extreme types of bonds—polar and non-polar.

	Polar (ionic)	*Non-polar (covalent)*
1.	Ionized	Not ionized
2.	Reactive	Not very reactive
3.	Ionizing solvents	Not ionizing solvents

4.	High dielectric constant	Low dielectric constant
5.	Associated molecules	Not associated
6.	Isomorphism	Isomerism
7.	High melting point	Low melting point
8.	High boiling point	Low boiling point
9.	Abnormal liquids	Normal liquids

Variable Oxidation States

The behaviour of the elements to show variable oxidation states is dependent mainly on valence electrons and the presence or the availability of certain electron orbitals. Alkali and alkaline earth metals normally do not show any variable oxidation states because of only s^1 and s^2 electrons in the outermost energy levels respectively. But since it is understood that the difference in energy between 3p and 4s energy levels is less than that between 2p and 2s, a transfer of electron from 3p to 4s is possible giving an excited state with corresponding increase in bonding orbitals in compound formation. In addition, the 3d levels are also available which permit an increase in bond formation. For example, the behaviour of fluorine and chlorine are quite different as regards compound formation. Fluorine is always monovalent, whereas chlorine gives a series of compounds with oxygen, such as Cl_2O, Cl_2O_3, ClO_2 etc. The variable oxidation states of chlorine occurs due to the excitation of 3p electrons to 3d and 4s energy levels. This situation does not exist for fluorine. Similarly, oxygen is always divalent whereas sulphur has variable oxidation of –2, +4, +6, as in H_2S, SO_2 and SO_3 or SF_6 respectively.

In the case of the transition elements such as Fe (26) and Cu (29), the variable oxidation numbers arise due to the loss of electrons from the 4s as well as 3d levels. Thus—

Fe — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

Fe^{+2} — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$ ($4s^2$ lost)

Fe^{+3} — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$ ($4s^2$ and one electron from 3d lost)

Cu — $1s^2\ 2s^2\ 2p^6\ 2s^2\ 3p^6\ 3d^{10}\ 4s^1$

Cu^{+1} — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ ($4s^1$ lost)

Cu^{+2} — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$ ($4s^1$ and one electron from 3d lost)

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If electronic excitation, involving the unpairing and increase in the number of unpaired electrons, requires an expenditure of energy which is less than the bond energies, a variable oxidation states is possible. If, on the other hand, the endothermic electronic excitation energy is greater than the exothermic combination of the atoms, the element will show a single oxidation state.

Other Types of Chemical Bond

The Metallic Bond : The properties of metals and alloys, such as lustre, hardness, tensile strength, malleability, electrical conductivity, heat conductivity etc. are to be explained in terms of a special type of bond known as *metallic bond.*

A number of theories have been put forward to explain the structure and bond systems in metals and alloys. Most metals form crystals in which each atom is surrounded by as many neighbours as is geometrically possible, usually 8 and 12. A number of geometrical shapes of crystals arise due to the various ways of packing. The atoms of metals consist of electrons and positive nuclei. There are not enough valence electrons to create electron-pair bonds between the atoms, since each atom is surrounded by eight or twelve neighbours. It is assumed that the valence electrons are free to pass from one atom to the other and is not associated with a single atom. These mobile electrons serve to hold the atoms together and constitute what is known as *"metallic bond."*

The metallic bond thus appears to be a modified form of covalent bond in which the freely moving electrons resonate between the atoms throughout the crystal lattice. The characteristic properties of metals, such as high lustre, high electrical and thermal conductivity etc. are due to these mobile valence electrons.

The electron-sea model : In metals the electrons are not tied down to a particular pair of atoms as in covalent bond, but are spread out over a relatively larger regions in the crystal lattice. This gives rise to the electron-sea model of metallic bond. The metal thus consists of positive nuclei immersed in a sea of mobile electrons. The metal ions are thus held together by a sort of electron glue. An schematic diagram of electron-sea model of Cs and Ba are shown in Fig. 2—30.

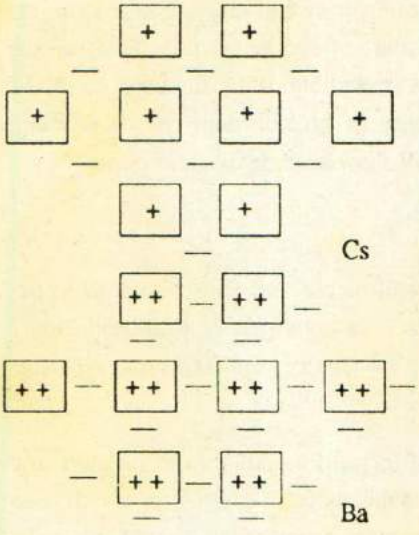


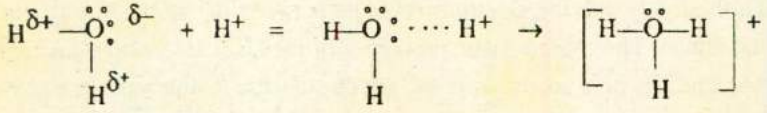
Fig. 2—30. Schematic diagram of electron sea model of Cs and Ba.

Dipole Bond : In some molecules the bond is partly covalent and partly ionic. Thus H_2O and HCl have appreciably polar character due to charge displacement in their molecules. This displacement or separation of charge in a molecule is known as "dipole moment" and is defined as the charge on one of the atoms multiplied by the distance (d) between the charges. Thus in HCl, the dipole moment (μ) is given by equation, $\mu = d.\delta^+$. The origin of the dipole moment lies in the difference in electronegativity of the two atoms forming the bond as explained later.

$$H^{\delta+} \overset{d}{\text{———}} Cl^{\delta-} \qquad \mu = d.\delta^+$$

Such molecules have tendency to form bonds with ions or diploes of opposite electrical charges and are known as dipole bonds. Thus—

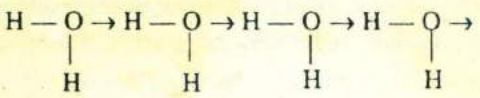
$$H_2O + H^+ = [H_3O]^+$$



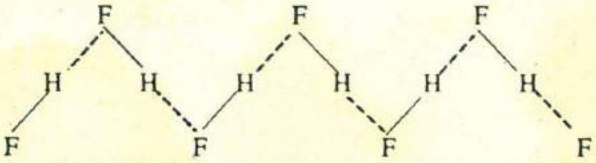
Similarly,

$$I^- + I_2 = [I_3]^-$$

The Hydrogen Bond : When hydrogen forms a bridge between two electronegative atoms of adjoining molecules, it is said to form a "hydrogen bond". Thus the familiar example of water molecules which are polar in character have hydrogen bonds indicated by arrows :



Similarly, in HF, the small electronegative F atoms are joined by hydrogen bonds. The broken lines indicate hydrogen bonds.



The hydrogen bond is primarily electrostatic in nature. It can not be regarded as a covalent bond since H has only one electron in its orbital and hence cannot give rise to electron-pair bond.

Hydrogen bond exists only between highly electronegative atoms, such as F, O, N etc. involving H atom.

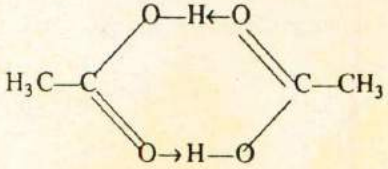
The presence of hydrogen bond confers unusual properties to molecules. Thus the boiling points of H_2O and HF are abnormally high because of hydrogen bonding as compared to other members of each series given in Table 2.3.

Table 2.3. Boiling points of some related compounds (°C).

Group V		*Group VI*		*Group VII*	
NH_3	–33	H_2O	+100	HF	+19
PH_3	–85	H_2S	–60	HCl	–85
AsH_3	–55	H_2Se	–42	HBr	–67
SbH_3	–17	H_2Te	–2	HI	–35

Association of the polar molecules is responsible for the abnormally high boiling points in HF and H_2O. This behaviour is due to the fact that energy is required to overcome the hydrogen bonds holding the atoms together in the associated molecules. The abnormally high dielectric constant of H_2O is again due to association of large number of polar molecules and has the dissolving

power for many ionic substances and also some organic substances containing OH groups, such as alcohol, sugar and some acids. The dissolution of these organic substances in water is primarily due to the hydrogen bonding. Hydrogen bond also occurs in many organic substances as in acetic acid which is dimerized.



Hydrogen bond is a relatively weak bond and measures approximately to only 5—10% of a covalent bond in strength. The hydrogen bond arises due to the attraction of positively charged proton by the negative electrons of two different atoms which are very electronegative. Intramolecular H-bonds occur in many molecules such as ortho-nitrophenol etc.

Van der Waal's Forces : All molecules and atoms when in close contact exert an attraction for one another. This attraction is very weak and has its origin in electrostatic attraction of the positive nuclei of one molecule for the electron cloud of another molecule in contact with each other. In the case of molecules having symmetrical charge distribution, some amount of inter-molecular attraction arises due to induced dipoles. The attraction of molecules or atoms for one another produces the van der Waal's forces which is electrostatic in nature.

Van der Waal's forces are very weak forces. Crystals having this inter-molecular forces are soft and melt at a very low temperature. The magnitude of the van der Waal's attraction increases with increase in the number of electrons per molecule. The van der Waal's forces cause the inert gases and halogen to become liquid and solid when the temperature is lowered considerably to bring the atoms and molecules of gases very close to each other.

QUESTIONS AND PROBLEMS

1. Write a note on the Electronic Theory of chemical bonds giving suitable examples.
2. Write short notes on:—
   (a) Covalent bond.
   (b) Dependence of physical and chemical properties on bond types.

(c) Variable oxidation states.

(d) Electrovalent and covalent compounds.

(e) Coordination bond.

(f) Difference between 'ionic' and 'covalent' bonding.

3. Give a brief account of the modern concept of chemical bonds. How are the properties of substances dependent on the bonds operating between their atoms ?

4. Write a concise account of what you understand by the electronic theory of chemical bond. Illustrate your answer with specific examples.

5. Discuss the connections of the electronic structures of positive and negative ions to that of the inert gases.

6. What is the physical and chemical differences between an atom of iron and ferrous and ferric ions.

7. When is the formation of coordination bond possible ? Give an example.

8. Show the electron distribution in the structural formula of the following molecules (write the Lewis structure):—

(a) $POCl_3$; (b) H_2SO_4; (c) HNO_3; (d) N_2O_4; (e) BF_3; (f) NH_4OH; (g) N_2; (h) $HClO_3$; (i) $HClO_4$; (j) $HClO_2$; (k) HClO; (l) O_2.

9. Write notes on :—

(a) Hybrid bonds; (b) σ and π bonds; (c) Directed bonds; (d) Molecular orbital theory; (e) Limitation of ionic and covalent bonds.

10. Discuss the bonding character of the elements N and P with special reference to their positions in the Periodic Table and to their oxides and hydrides.

11. What types of chemical bonds are recognized in modern electronic concept ? Give examples illustrating each type and write down their electronic formula.

12. (a) Explain the electron distribution in the compounds: magnesium iodide and lithium chloride.

(b) Show that methane, carbon tetrachloride and water contain covalent linkages among their respective atoms.

(c) Prove that hypochlorous acid and phosphorus oxychloride contain coordinate bonds in their molecules.

13. Mention how the distribution (of electrons in atoms) contributes towards the nature of bonding.

Explain the bonding in NaF, CO and $Co(NH_3)_6Cl_3$.

14. How far the knowledge of the electronic configuration of atoms of rare gases has helped in explaining the formations of chemical bonds ?

15. Indicate the different types of bonds that are present in the following compounds :—

(a) NaCl; (b) $(H_2O)_x$; (c) $[Cu(NH_3)_4]Cl_2$.

Discuss the modes of formation of any two types of bonds.

16. Write a brief notes on:—

(a) Coordination bond, (b) Variable oxidation states.

17. (a) Discuss the different types of bonding that are recognised in modern chemistry. Illustrate your answer with suitable examples.

(b) Explain the terms "electronegativity of elements" and "variable oxidation state

18. (a) Enumerate the fundamental ideas of the electronic theory of chemical bonds and different bond types.

(b) Explain hybridization of orbitals, bond strength and bond angle.

19. Discuss the different types of bonding that are commonly encountered in chemical compounds. Illustrate your answer with examples.

What is meant by hydrogen bond?

20. Discuss the bonding and properties of water.

21. Write short note on electronegativity of elements.

22. What are σ– and π- bond ?

23. What do you understand by bond order. Calculate the bond order in the following molecules N_2, O_2, He_2, NOF_2

24. Indicate the relationship of bond order with the properties of the molecules.

25. Discuss bond hybridizations in the compounds of non-transition elements giving examples of inorganic species only.

26. Compare the Valence Bond and Molecular Orbital Theroires of the chemical bonds.

CHAPTER 3

THE SIZES OF ATOMS AND IONS

The sizes of atoms, ions and molecules have important relationships with their chemical behaviour.

Atomic sizes are expressed in Angstrom unit (1 Å = 10^{-8} cm). We can get some idea of the range of atomic size by noticing one of the smallest atoms, F, having radius of 0.72 Å), while one of the largest, Cs, has a radius of 2.35 Å. It may be noted that since an atom is made up of a compact nucleus and a diffuse electron cloud, the size of an atom may be considered primarily as the space occupied by its electron cloud. Hence it is the electronic structure which actually governs the sizes of atoms and ions.

Sizes of Atoms

Atomic and covalent radii : The size of an atom depends upon two factors : (1) The positive charge on the nucleus and (2) the number of occupied electron levels about the nucleus. By keeping these two factors in mind we can easily visualize the relative sizes of the atoms of the various elements. Thus it may be inferred that the size of an atom is determined by the cloud of 1 to 105 electrons from H to Ha which occupy a space whose diameter is of the order of 50,000 to 100,000 times greater than the diameter of the nucleus. The probability of finding an electron at a given distance from the nucleus is maximum at a definite distance which is characteristic of the energy level occupied by the electron. At any given time, however, the electron may be further from the nucleus or closer to it. Hence the size of an isolated atom cannot be expressed in any precise way. Therefore, we measure the distance between two nuclei when two atoms approach each other and then calculate the atomic sizes of the two atoms from the inter-nuclear distances. Thus the size of the isolated

atoms and those obtained in purely covalent compounds of the same atoms are supposed to be identical, Therefore, the *atomic radii* and *covalent radii* of elements have the same definition.

Bond Length

The inter-nuclear (or inter-atomic) distance between two bounded atoms of the same kind is called the Bond Length. This is considered to be the sum of two lengths, called the Covalent Radii of the atoms. The bond length in Cl_2 or Cl–Cl has been determined to be 1.98 Å. One half of this value in chlorine molecule can be attributed to each chlorine atom. Thus the covalent radius of each chlorine atom is 0.99 Å. In diamond crystal, each carbon atom is bound covalently to four other C atoms having inter-nuclear distance of 1.54 Å between two C atoms. In the elementary silicon which also has the diamond structure, the Si—Si distance is 2.34 Å. Thus the covalent radius of carbon is 1.54/2=0.77 Å and for silicon 2.34/2 = 1.17 Å. From these figures it is possible to calculate correctly the bond lengths in compounds containing carbon and silicon. Thus C—Si distance in tetramethyl silane, $(CH_3)_4Si$, is calculated to be 0.77+ 1.17 = 1.94 Å which agrees very well with the experimental value of 1.93Å. The following methods are generally used for determining the atomic or covalent radii: (1) X-ray diffraction, (2) Electron diffraction, (3) Neutron diffraction and (4) Absorption spectra etc.

The covalent radius of an atom varies from element to element, but the radius also depends on the number of electrons shared in a covalent bond. Thus, the inter-nuclear distance and the covalent radii are largest for a single bond, smaller for double bond and smallest for triple bond. Table 3.1 shows the values of covalent radii of some atoms forming single, double and triple bonds.

We can summarise the relationship between atomic size and the Periodic Table as follows:

1. The size of an atom decreases with increasing atomic number within any one periodic series. It will be noted that this decrease is due to two factors which control the atomic size, namely, (i) the positive charge on the nucleus and (ii) the number of occupied electron level about the nucleus. Hence the atoms in the first series of the Periodic Table will be of small size because there is one electron level. The smallest atom will also be

that one in the first series that has the greatest nuclear charge. This is He which has nuclear charge +2 and only one occupied electron level. The largest atom will have the small nuclear charge but with the greatest number of occupied electron level. Cs is the largest atom because it meets these requirements.

Table 3.1. Normal covalent radii of some atoms in Å units.

Elements	*Single bond*	*Double bond*	*Triple bond*
H	0.30	—	—
B	0.88	0.76	0.68
C	0.77	0.67	0.60
N	0.74	0.62	0.55
O	0.73	0.55	—
F	0.64	—	—
Si	1.17	1.07	1.00
P	1.10	1.00	0.98
S	1.04	0.94	—
Cl	0.99	—	—
Ge	1.22	1.12	—
As	1.21	1.11	—
Se	1.17	1.07	—
Br	1.14	—	—
Sn	1.40	1.30	—
Sb	1.41	1.31	—
Te	1.37	1.27	—
I	1.33	—	—

2. Just after the inert gas structure, the extra electron goes into a new quantum level and hence the alkali metals have much greater atomic radii than the inert gases.

3. The transition elements in which the **d** and **f** levels are gradually filled, the atomic and ionic radii decrease with the increase in the atomic number in the same series. This is because the additional electron goes to the inner energy level closer to the nucleus which exerts greater attraction.

4. The electron cloud around an atomic nucleus "shields" or "screens" the nucleus and cancels the nuclear charge. All the electrons in an atom do not possess the same effect for shielding the nucleus. The fraction of the nuclear charge that in effect is cancelled by an electron is called the screening constant. Effective nuclear charge *of an element is obtained by* subtracting the sum of the screening values of the individual electrons in the cloud from the actual charge on the nucleus. Progressive increase in the atomic number across the Periodic Table leads to progressively greater effective nuclear charge. This gives rise to the decrease in the atomic size (atomic radius).

Ionic Radii and Energy Relationship

Formation of positive and negative ions from neutral atoms involves energy. It may easily be visualized that the size of an atom decreases when one or more electrons are removed from the electron cloud of the atom to form a positive ion. In order to remove the electron from an atom, energy will be required and the quantity of this energy depends upon two factors : (1) the size of the atom from which the positive ion is formed and (2) the number of electrons that must be removed to form the positive ion.

On the other hand, in order to form a negative ion, one or more electrons must be added to the electron cloud of an atom. When a neutral atom gains one electron to form a negative ion, a definite amount of energy is released. It may be easily visualized that the size of an atom increases when one or more electrons are added to it to form a negative ion. The same factors that influence the readiness of atoms to form positive ions, also influence the formation of negative ions.

The closer an electron is to the nucleus, more strongly it is attracted. This means that less energy is required to remove electrons from the outer energy level of a large atom than from a small atom. It is easier to form positive ions from a large atom than from a small atom. In the case of the formation of negative ions, a small atom accepts electron more readily than a large atom. Hence the smaller atoms form negative ions more readily than the larger atoms.

Ionization Energy (Potential) and Electron Affinity

In this connection we come across the terms Ionization Energy (Ionization Potential) and Electron Affinity.

Ionization Potential : Ionization energy of an element is the energy required to remove one electron from the electron cloud of an isolated atom obviously from the outermost energy level. The ionization energy is measured in the units of electron volts (ev) or kilocalories per gramme atom (Kcal/g. atom). An electron volt has been defined as the energy required to raise an electron through a potential difference of 1 volt, or the energy released when an electron drops through a potential difference of 1 volt.

The ionization potential is also a fundamental property of an atom. For each successive electron that is removed, a progressively greater amount of energy is required. In the formation of a singly charged positive ion, the ionization energy is simply the energy required to remove the most loosely held electron from the outermost electron level of the atom. This is referred to as the first ionization energy (potential). For the removal of the second electron from the singly charged positive ion, additional energy is required and this is known as the second ionization potential. It is easily seen that the second ionization energy will be greater than the first ionization energy and that there is a limit to the removal of electrons for the formation of positive ions.

To remove electrons from atoms or ions having inert gas structure considerable amount of energy is required to pull the electron out of a filled energy level. This is the reason why dipositive ions of alkali metal do not exist in nature.

In general, as the number of electrons that must be removed continue to increase, the formation of positive ion becomes progressively more difficult.

Table 3.2 gives the values of first ionization potential both in ev and Kcal/g. atom of alkali metals (1 ev = 23.06 Kcal/mole or 6.02×10^{23} ev = 23.06 Kcal).

Table 3.2. Ionization potentials of alkali metals.

Elements	*Ionization Energy (potential) ev*	*Kcal/g. atom*
Li	5.4	124
Na	5.1	118
K	4.3	100
Rb	4.2	95
Cs	3.9	89

The ionization energies of alkali metals decrease as the size of atoms increases. The successive increase in the amount of energy required to remove more than one electron from an atom is given in Table 3.3 in Kcal/g. atom of Mg, Al and Cu.

Table 3.3. Ionization potential (Kcal/g. atom).

Elements	*First Ionization Potential*	*Second Ionization Potential*	*Third Ionization Potential*
Mg	Mg^{+} 176	Mg^{+2} 246	
Al	Al^{+} 138	Al^{+2} 434	Al^{+3} 656
Cu	Cu^{+} 178	Cu^{+2} 468	

When the first ionization energy of all the elements are plotted against the atomic numbers, a curve is obtained which shows the periodic variations in this fundamental property with atomic numbers. A part of the curve is shown in Fig. 3—1.

The peaks of the curve showing the maximum amount of ionization energies are occupied by the inert gases, the alkali metals naturally occur at the bottom troughs of the curve. It may be noted that the ionization potential as indicated in the curve increases somewhat irregularly in proceeding along a series

of elements in the Periodic Table. The irregular increase may be attributed to the following main factors : —(1) nuclear charge, (2) number of outermost electrons

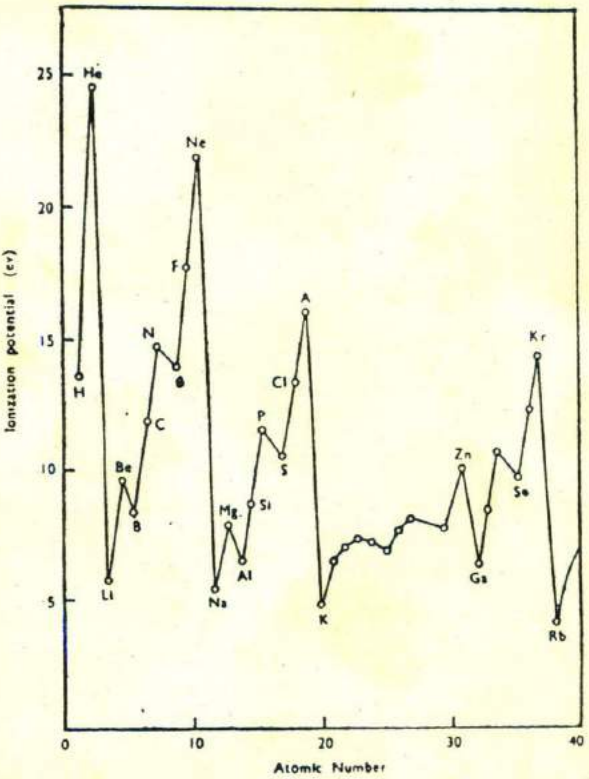


Fig. 3—1. The first ionization potentials of elements from H to Rb.

and (3) the atomic radii. Table 3.4 gives the values of the first ionization potential of the elements of the first series (row) of the Periodic Table.

Notice the decrease in ionization potential of boron which is due to the presence of a single (unpaired) electron in 2p level. Less amount of energy is required to

Table 3.4. Ionization potential of the first period. (ev)

Elements	*Nuclear charge*	*Electrons configuration*	*No. of electrons in the outermost level*	*Atomic Radii Å*	*First Ionization Potential (ev)*
Li	3	$1s^2\ 2s^1$	1	1.52	5.39
Be	4	$1s^2\ 2s^2$	2	1.07	9.32
B	5	$1s^2\ 2s^2\ 2p^1$	3	0.89	8.30
C	6	$1s^2\ 2s^2\ 2p^2$	4	0.77	11.26
N	7	$1s^2\ 2s^2\ 2p^3$	5	0.70	14.54
O	8	$1s^2\ 2s^2\ 2p^4$	6	0.66	13.64
F	9	$1s^2\ 2s^2\ 2p^5$	7	0.64	17.42
Ne	10	$1s^2\ 2s^2\ 2p^6$	8	1.12	21.56

remove one electron from $2p^1$ of B atom as compared to the removal of an electron from paired-up $2s^2$ of Be or $2p^2$ of C. The first ionization potential of B shows a decrease in value (Fig . 3—1). Since a half-filled $2p^3$ level of N is more stable than $2p^4$ of oxygen, the removal of one electron from $2p^4$ requires less energy. Hence the ionization potential of oxygen is less than that of nitrogen. Similar drops in ionization potential occur for other elements (Fig. 3—1).

Electron Affinity: Electron affinity of an atom may be defined as the energy released when a neutral isolated atom in the ground state takes up 1 electron to form a negative ion.

The readiness of atoms to form negative ions also depends upon two factors: (1) the size of the original atom and (2) the number of electrons involved in ion formation. The smaller the atom and smaller the negative charge on the resulting ion, the more readily a negative ion is formed. The fundamental causes of this behaviour of atoms are probably very complex. It can be easily visualized that the nucleus of the smaller atom exercises a greater attraction on available electrons than does the nucleus of the larger atom.

Taking the formation of halide ions from halogens, it is known that atoms o the halogen family increase in size from fluorine to iodine. The smallest fluorine

takes up one electron most readily, the largest iodine takes up least readily. Thus the tendency of the formation of negative ions decreases markedly from fluorine to iodine. Similarly, this is the case in the series O, S, Se and Te.

Once a halogen has accepted an electron to form a negatively charged ion, it will show reluctance to accept further electrons.

It is also noticed that a singly charged negative ion forms more readily than a doubly charged negative ion. Taking the examples of Na, Mg, Al, Si, P, S and Cl, it is known that only the last two, namely, S and Cl, form negative ions readily. Sulphur takes up 2 electrons in its outer energy level to produce the electronic configuration of argon. Chlorine takes up only one electron for the same reason but much more readily than sulphur atom. The formation of phosphide ion P^{-3} takes place less readily. In fact, *simple* negative ions with a charge greater than -2 are very unusual.

In each case the negative ions are always larger than the neutral atoms from which they are formed.

Ionic Radii

The size of an atom decreases when one or more electrons are removed from its electron cloud to form a positive ion and increases when electrons are taken up by the atom. Hence it is possible to frame a general rule to the effect that the ionic radius of any cation is smaller than the radius of the neutral atom, whereas the radius of the anion is always greater. The change in the size of atoms after removing one or more electrons are shown below in Å.

Fe — 1.26	Fe^{+2} — 0.75	Fe^{+3} — 0.60
Mn— 1.29	Mn^{+2} — 0.80	Mn^{+4} — 0.52
Pb — 1.75	Pb^{+2} — 1.21	Pb^{+4} — 0.84

By X-ray methods it has been possible to determine the distance between the nuclei of two oppositely charged adjacent ions in an ionic compound. The distance between the neighbouring positive and negative ions in contact with each other in a crystal is called the inter-ionic distance. It has been assumed that ions act as spheres of almost constant radii and the measured inter-ionic distance

R is the sum of the radii of two spheres, r^+ and r^-, in contact with each other as shown in Fig. 3—2.

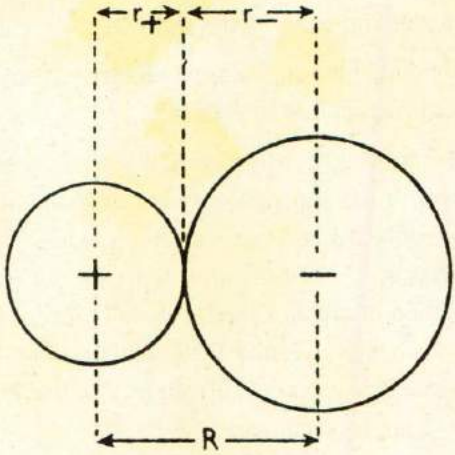


Fig. 3—2. Inter-ionic distance and ionic radii.

If R is measured, say, by X-ray diffraction method and either the radius of the positive ion r^+, or the radius of the negative ion r^- is known, the unknown radius can be easily calculated from,

$$R = r^+ + r^-$$

The ionic radii of elements exhibit periodicity or periodic variations as in the case of atomic radii.

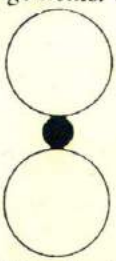
The size of the ions is a physical property but this property is closely connected with the chemical properties of the elements. The chemical bonds among the elements are mostly dependent upon or related to the sizes of ions. The acid or alkali behaviours of cations in aqueous solutions are related to their ionic sizes. Similarity and dissimilarity of properties among groups of elements are influenced by ionic size and so on. Substitution of one ion by another in a crystal depends on the ionic radii of the species concerned. As a matter of fact, the ionic size is one of the most important factors which determines the structure and properties of substances.

Radius-Ratio Effect in Ionic Crystals : The geometrical shape of a crystalline solid is largely determined by the ratio of the ionic radii of the

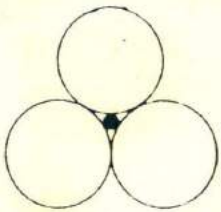
positive and negative ions. This ratio also determines the coordination number of the central ion. In ionic crystals each ion tends to surround itself with as many oppositely charged ions as possible from geometrical considerations, and the number of the nearest neighbours is the coordination number of the central ion in the crystal.

Crystal Coordination Number : Thus the crystal coordination number of a positive ion in a crystal may be defined as the number of negative ions arranged in a symmetrical manner around the positive ion and in contact with it.

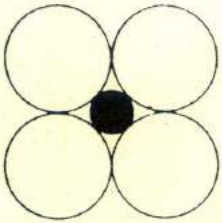
It has been assumed that ions are perfect spheres, and it is possible to calculate the minimum radius of an ion around which other ions of unit radius can be arranged. For instance, the ratio r^+/r^- having a value of about 0.15 indicates that only two anions can be arranged about a cation so that the three ions are in contact with each other. Similarly, the ratio r^+/r^- having values from 0.15 to 0.22 indicates that three anions could be in contact with each other enclosing a central cation giving a 3-fold symmetrical coordination. Fig. 3—3 shows some of the arrangements. Notice the different sizes of the central cations (black spheres).



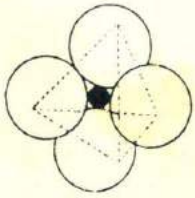
Two-fold coordination
(Linear)



Three-fold coordination
(Triangular)



Four-fold coordination
(Planar)



Four-fold coordination
(Tetrahedral)

Fig. 3—3. Relative sizes of the ions and coordination number.

Table 3.5 shows the dependence of coordination number and geometrical shapes on the radius-ratio r^+/r^- in general.

Crystal Lattice : A crystal lattice is made up of an infinite repetitions of a small group of ions in three-dimensional pattern.

Solid ionic compounds consist of crystal lattice which is built up by the combination of a regular array of ions in which each ion is surrounded by a definite number of ions of opposite charges. Thus in the ionic lattice of sodium fluoride, the Na—F distance is 2.31 Å and of this 0.95 Å is the radius of the fluoride ion. The radius ratio, $\frac{rNa}{rF}$, is 0.69, and hence the crystal lattice possesses octahedral or 6-fold coordination in which each sodium ion is surrounded by six fluoride ions and each fluoride ion is surrounded by six sodium ions. NaCl has the same crystal structure.

Table 3.5. Radius-ratio effect.

Ratio $\frac{r^+}{r^-}$	*Coordination Number*	*Geometrical shape*
Upto 0.15	2	Linear
0.15 — 0.22	3	Triangular
0.22 — 0.41	4	Tetrahedral
0.41 — 0.73	4	Planar
0.41 — 0.73	6	Octahedral
0.73 and above	8	Cubic

The small group of ions which is repeated in a crystal lattice in three-dimensional pattern is known as a *unit cell*. The unit cell is thus the smallest portion of the crystal lattice which has all the various kinds of symmetry which characterise the crystal. A unit cell cannot exist singly since all the unit cells in a crystal lattice have common boundaries.

Lattice Energy : The lattice energy of an ionic compound is defined as the energy released when the crystal lattice is formed by combination of requisite number of free gaseous positive and negative ions in an ionic crystal to give one mole of the compound. Conversely, it may also be defined as the energy required

to break the crystal lattice in order to separate two positive and negative ions to infinite distance.

During the formation of an ionic compound it can be seen that the processes involved are; (i) The formation of a positive ion by removal of one or more electrons from a neutral atom and (ii) the formation of negative ions by the neutral atoms by acquiring electron. The first process involves the ionization energy and the second process involves the electron affinity of the atoms. The ionization energy required for the formation of positive ion and the energy released during the negative ion formation are opposed to each other. As a general rule, the ionization energy is much greater than the electron affinity. When the difference between the two values for given atoms is small, the chemical combination results in the formation of ionic compound. When the difference is large, the compound produced will be either partly or almost completely covalent.

But the formation of an ionic compound is not only dependent upon the difference between the amounts of ionization energy and electron affinity but also upon the lattice energy of the compound. Thus in chemical reactions leading to ionic compounds the energy required to produce the positive ion must be supplied by the release of energy in another part of the reaction. For instance, the formation of the solid from the ions would provide energy through the action of electrostatic forces, i. e., the lattice energy is available to supply the difference between ionization energy and electron affinity. It may be noted that ionic compounds are not made up of individual molecules. Th crystal lattice is built of a cluster or ion pairs in the form of groups. The number of groups around a central ion (crystal coordination number) is determined by the radii of the respective ions involved. Measurements of lattice energy have been made by means of a cyclic process known as energy cycle, specifically known as Born-Haber Cycle. as given in Fig.3—3 in the case of NaCl :

E = Electron affinity for Cl, I = ionization energy of Na (gas), S = sublimation energy of Na (solid), D = dissociation energy of Cl_2 and U = Lattice energy of the formation of NaCl (solid).

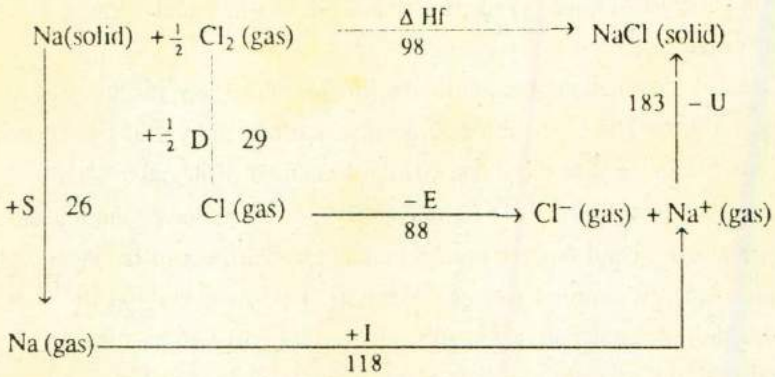


Fig. 3—3. Born-Haber cycle for NaCl

The heat of formation ΔHf of NaCl from Na (solid) and Cl_2 (gas)

$$\Delta Hf \equiv E - I - S - {}^1/_2\, D + U$$

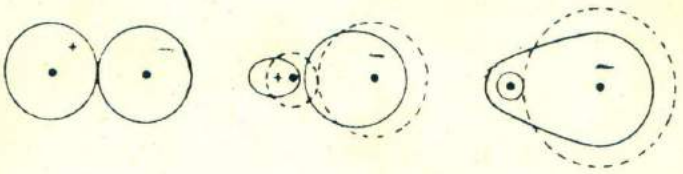
$$\text{Lattice Energy } U = \frac{-121.4nZ^+Z^-}{r^+ + r^-}\left(1 - \frac{0.0345}{r^+ + r^-}\right)$$

The Relationship Between Ionic and Covalent Bond

Covalent Character of Ionic Bond : In most cases the distinctions between ionic and covalent bonds are not very sharp. It may be remembered that ionic bond and covalent bond are extreme types of electronic interaction. Many chemical compounds involve a complex blending of both types of bonds. Hence the chemical bond may be considered as partly ionic and partly covalent and the relative degree of each type of bonding varies from compound to compound.

The difference between ionization energy of positive ions and electron affinity of negative ions indicate the nature of bounding between the two atoms. A small difference indicate ionic bond whereas a large difference points to covalent bond.

In a molecule containing two dissimilar atoms, displacement of electric charge takes place. This is much more prominent in the case of atoms of different sizes. Thus when a small positive ion comes very close to a large negative ion, the negative ion may be pulled out of shape or distorted as shown in Fig. 3—4. The distorted ion is not symmetrical but its centres of negative and positive charges have been displaced.



Separate ions
Inter-ionic attractions
(ionic bond)

Some distortion
Intermediate
bond

Maximum distortion
leading to
covalent bond

Fig . 3—4. Distortion of electron clouds.

Polarisation : The distortion of the electron cloud of a negative ion by a positive ion in a molecule is known as "polarisation." Molecules containing distroted electron clouds having separate centres of positive and negative electricity are known as polar molecules. The bonds between polarised ions or atoms are known as *polar bonds*. An extreme case of polarity is represented by an ionic compound such as sodium chloride ($Na^+ — Cl^-$) in which the sodium ion is almost completely positive and chloride ion is almost completely negative, and hence the bond is purely ionic. But if the size of the anion is much larger than that of the cation, the ionic bond has tendency to show covalent character because of polarisation. For instance, AgF is an ionic compound, soluble in water and colourless, whereas AgI is, to a great extent, covalent compound insoluble in water and coloured. In general, the greater the extent of polarisation, the greater is the covalent character of the chemical bond.

Fajans' Rule : Polarisation of ions depends upon a number of factors. According to Fajans' rule, the greatest effect of polarisation is produced in molecules having,

(i) Small size of cation,

(ii) Large size of anion,

(iii) High charge on either cation or anion,

(iv) Cations with electrons in **d** and **f** orbitals.

The overall effect of the above factors produce increased degree of covalent bond in ionic compounds.

Taking melting point as a criterion to distinguish between ionic and covalent bond, the comparison in Table 3.6 gives some idea about the effects of charge and size and distortion in the respective molecules according to the Fajans' rule. It may also be remembered that some covalent substances, such as diamond and silica, have high melting points because they occur as giant molecules.

Table 3.6. Melting points and Fajans' Rule.

Molecules	*m. p. (°C)*	*Bond Type*	*Polarisation due to*
MgF_2	1396	Ionic	—
MgI_2	632	Less ionic	large I^-
$BaCl_2$	962	Ionic	—
$BeCl_2$	440	Almost covalent	Small Be^{+2}
NaCl	801	Ionic	—
$SnCl_2$	247	Less ionic	Sn^{+2}
$SnCl_4$	–30	Covalent	Sn^{+4}
$CuCl_2$	422	Less ionic	Cu^{+2} (with d electron)
KCl	776	Ionic	—
$TiCl_4$	–30	Covalent	Ti^{+4}

Electronegativity

"Electronegativity has been defined as the power of attraction by an atom for electrons in a molecule." The atom which has greater attracting power for the electrons in a molecule is said to be strongly electrophilic or electronegative or it is said to have a high electronegativity. A covalent bond between like atoms may be regarded as a true covalent bond since both the atom exhibit equal power of attraction for the electrons in the molecule.

The polarity of a covalent bond depends primarily on the difference in the electronegativity of the two elements forming the bond. Changes of the polar character of covalent bonds can be observed in the following series of isoelectronic molecules (molecules having the same total number of electrons).

CH_4 NH_3 OH_2 FH

The C— H, N— H, O — H and F — H bonds are increasingly more polarised so that F is more electronegative than O which, in turn is more electronegative than N and C is least electronegative. The electronegativity of these atoms are in the order of

$$F > O > N > C$$

The term electronegativity is connected with a number of properties which may characterize an element and the behaviour of its compounds. Electronegativity of an element is influenced by the size of the atom and by the number of electrons required for it to form a stable ion.

By considering various types of experimental data Pauling has made a quantitative calculations of electronegativity values of various elements. The relative electronegativity values of some of the more common elements are given in Table 3.7. These values are based upon an arbitrary scale. Notice that the non-metals have higher electronegativity values than the metals. Thus, fluorine, the most chemically active non-metal, has highest electronegativity (4.0) and cesium, the most chemically active metal (with the possible exception of francium), has the lowest electronegativity (0.7). Because the metals have relatively low electronegativities and tend to assume a positive charge in compounds, they are generally called electropositive and non-metals are known as electronegative.

Calculation of Electronegativity Values : Two main methods for calculating the electronegativity values of elements are (a) Pauling's method and (b) Mulliken's method.

Table 3.7. Electronegativity of some elements (Pauling Scale).

Li	Be	H	B	C	N	O	F
1.0	1.5	2.1	2.0	2.5	3.0	3.5	4.0
Na	Mg		Al	Si	P	S	Cl
0.9	1.2		1.5	1.8	2.1	2.5	3.0
K	Ca			Ge	As	Se	Br
0.8	1.0			1.8	2.0	2.4	2.8
Rb	Sr			Sn	Sb	Te	I
0.8	1.0			1.8	1.9	2.1	2.5
Cs	Ba			Pb	Bi		
0.7	0.9			1.8	1.9		

(a) *Pauling's method :* This is based on the estimated contribution of the ionic nature A^+B^- of bond between two atoms A and B to the actual bond between A and B (AB).

If the actual bond energy measured experimentally between A and B = ΔH and the bond energy for a truly covalent bond = E_{AB}, then the resonance energy caused by the ionic character of the bond = $\Delta H - E_{AB}$. The value of E_{AB} was obtained from either the arithmatic or geometric mean of the bond energies of the bonds A—A (E_{AA}) and B—B (E_{BB}) respectively so that

$$E_{AB} = \frac{E_{AA} + E_{BB}}{2} \quad \text{or} \quad E_{AB} = \sqrt{E_{AA} \times E_{BB}}$$

The difference between ΔH and E_{AB} is the ionic resonance energy of bond A—B. This ionic resonance energy, designated as Δ, is large for molecules having widely different electronegativities.

If χ_A and χ_B are the electronegativities of element A and B respectively, then these were related to Δ by the relationship :

$$\chi_A - \chi_B = 0.208 \sqrt{\Delta}$$

Pauling arbitrarily fixed χ for H = 2.1 and for F = 4.0 in order to calculate the electronegativity values of other elements.

(b) *Mulliken's method :* According to Mulliken's definition, electronegativity of an atom is equal to the arithmatic mean of its electron affinity and its ionization potential.

Thus the electronegativity χ_A of atom A is given by the relationship :

$$\chi_A = \frac{I_A + E_A}{2}$$

where I_A is the ionization energy and E_A is the electron affinity of atom A.

This method is of limited value since the measurement of electron affinity is difficult, but has been found to be useful in explaining the ionic changes in bond hybridization. Thus the difference in the properties of sp, sp^2 and sp^3 hybridized carbon compounds can be readily explained.

Ionic Character of Covalent Bond

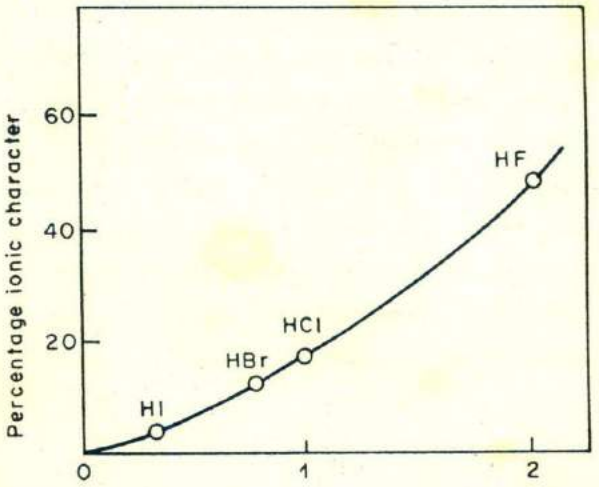
The calculated electronegativity values are in accord with chemical facts when the differences in electronegativity values are used as the basis for

comparison. A small difference in the electronegativity values of the two atoms forming the bond indicates almost equal sharing of electrons forming a non-polar type of bond (covalent bond). The larger the electronegativity difference, the more polar is the bond and charge separations between the atoms are greater resulting in pronounced ionic character. The amount of ionic character in the series of hydrogen halides indicates a decrease in the order of HF, HCl, HBr and HI as shown in Fig. 3—5. The charge separation in HF is much greater than that in HI. HCl and HBr are intermediate between HF and HI. H in, say, HCl, has a partial positive charge and Cl, a partial negative charge, represented as δ^+ and δ^- respectively.

$$\overset{\delta^+}{H} : \overset{\delta^-}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}} :$$

Thus HCl molecule has a strong polar covalent bond.

When a molecule contains a number of bonds, the charge separation is rather complex. Some schematic representations of the molecules showing the displacement of electron pair bond and partial charges are given in Table 3.8.



Difference in electronegativities $\chi_A - \chi_B$ of hydrogen and halogen.

Fig. 3—5. Relationship between ionic character and electronegativity.

Table 3.8. Charge separation in molecules.

Compound	*Electron-pair displacement*	*Partial charge displacement*
HBr	H : Br :	δ^+ δ^- H — Br
ICl	: I : O :	δ^+ δ^- I — Cl
H_2O	H : O : H	δ^+ $\delta^=$ H — O $H^{\delta+}$
H_2S	H : S : H	δ^+ $\delta^=$ H — S $H^{\delta+}$

Dipole Moments : One important physical property which is the result of charge separation in polar covalent compounds is dipole moment or electrical dipole moment. The extent of charge separation between two atoms in a molecule is measured by $\delta = \mu/de$, where δ is the bond length, e is the charge of an electron and μ is dipole moment of the bond. δ is a fraction of an electron charge and its quantity is such if $+\delta$ be placed on one atom and $-\delta$ on the other, the molecule would have the observed dipole moment μ. Distance between A and B = d. δ = fraction of charge on either A or B.

$$\begin{matrix} +\delta & & -\delta \\ A & \xleftarrow{\quad d \quad} & B \end{matrix}$$

Dipole moment provides an index of the polarity of a molecule; the greater the value of dipole moment, the greater is the polarity. The values of dipole

moments for hydrogen halides and the electronegativities of halogens are given below.

Hydrogen halide	*Electronegativity of halogens*	*Dipole moment* μ (Debye Unit)
HF	F = 4.0	1.91
HCl	Cl = 3.0	1.03
HBr	Br = 2.8	0.78
HI	I = 2.5	0.38

Thus from the electronegativity values, HF is the most polar of all hydrogen halides and has a large value for the dipole moment.

Resonance Structures

The polar covalent bond does not indicate the presence of both covalent and ionic bonds in the same molecule. The polar bond has been produced by the combination of different types of electronic interactions in certain proportions. In a molecule of HCl having largely a covalent bond but with some ionic character, the bond may be considered as a blend of covalent bond and ionic bond between H and Cl. Hence the bond is neither purely covalent, nor purely ionic but a blend of the two extreme types with varying proportions. (see Chapter 2 Page 85)

Bond Length, Bond Angle and Bond Energy

Bond Length : The distance between the centres of two nuclei of atoms connected by a chemical bond is known as bond length. The distance between two atoms or bond length in a molecule has been calculated by the use of the sum of covalent radii. The distance involved between two atoms or the bond length is very small and is generally expressed in terms of Angstrom units (1 Å $=10^{-8}$ cm). (See also page 106)

The bond lengths in molecules are measured by various methods, such as X-ray diffraction and spectroscopic methods. The bond lengths between two atoms bonded by a single covalent bond appear to be nearly constant. Thus C—Cl bond length in CH_3Cl, CH_3CH_2Cl, $CHCl_3$ and CCl_4 is almost 1.76 Å. Similarly, C—C single bond in many of the organic compounds is of the order of 1.54 Å.

If R_{AB} is the interatomic distance between two atoms A and B, it has been found that R_{AB} is equal to the mean of the bond lengths A—A and B—B. In other words, if r_A is the covalent radius of A and r_B the covalent radius of B, then

$$R_{AB} = r_A + r_B = \frac{R_{AA} + R_{BB}}{2}$$

Bond lengths between two atoms may also be designated as double or triple bond which are measured in similar manner as the single bond. Hence for atoms we can assign single, double and triple bond covalent radii. Radii of some atoms are given in Table 3.9. (See also Table 3.1)

Table 3.9. Single, double and triple bond covalent radii in Å unit.

Atom	*Single bond covalent radius*	*Double bond covalent radius*	*Triple bond covalent radius*
H	0.30	—	—
B	0.88	0.76	0.68
C	0.77	0.67	0.60
N	0.74	0.62	0.55
O	0.73	0.55	—
P	1.10	1.00	—
S	1.04	0.94	—
Cl	1.00	—	—

But there are factors which influence the bond lengths; for instance, the polarity of a covalent bond has tendency to decrease the bond length and hence the calculated value may be a little too large. Again, the increase in coordination number may increase the bond distance. Bond distance in molecules may also be influenced by resonance and electronic interactions of complex types and also the strength of bond varies for different reasons. Thus CO_2 the structure O—C—O is more appropriate since C uses **sp** hybrid and two π bonds due to overlapping between delocalized **p** orbitals.

Bond Angle : The angle between the directions of two bonds in a molecule is called the "bond angle".

A bonding electron pair is concentrated most strongly in the direction of the line joining the bonded atoms. These bonded atoms may be joined to a central atom and then each electron pair or pairs may form separate bond. The bond angle in molecules depend upon various factors, namely the charge distribution, geometry of the molecules, symmetry, hybridization etc. Some of these are shown below for normal molecules.

Bond hybridization	*Geometry*	*Bond angle*
sp	Linear	180°
sp^2	Triangular	120°
sp^3	Tetrahedral	109° 28′
sp^3d or dsp^3	Trigonal bipyramid	Basal — 120° Apical—90°
sp^3d^2 or d^2sp^3	Octahedral	90°
dsp^2	Square planar	90°

In most cases regular geometrical shapes are distorted for various reasons giving rise to the variation of bond angles.

Bond angles for some molecules and ions are given in Table 3.10. The geometry of the molecules have been discussed in Chapters 5 and 24.

Table 3.10. Bond angles of some molecules and ions.

Species	*Angle*	*Species*	*Angle*
CH_4	H—C—H 109°	SO_3	O—S—O 120°
NH_4^+	H—N—H 109°	NO_3^-	O—N—O 120°
H_2O	H—O—H 105°	NH_3	H—N—H 107°

Bond Energy : "Bond energy" is defined as the energy required to split the molecule into atoms. This may also be defined as the energy released in the formation of a molecule from atoms by assuming that the total energy is composed of separate contributions from each bond. Bond energy may be determined from the spectrum or by measurement of equilibrium constants for dissociation of the molecules at high temperatures. When there is only one formulation of covalent bond in a molecule, the bond energy calculated by applying summation of Hess' Law agrees well with the experimental determination, for instance, in CH_4, but not in C_6H_6. Bond energy, therefore,

gives indication of the type of bonding involved and also points out the existence of single, double or triple bonds in a molecule. The bond strength resulting from a variety of reasons throws much light on the stability of molecules, and are of great practical applications.

For example, Pauling's values of electronegativities of elements have been derived from the experimentally determined values of bond energies. The bond energy of Cl—Cl bond is the energy required to separate the molecule of Cl_2 into two atoms (2Cl), not ions. Similarly, bond energy of H_2 is the energy required to split H_2 into two atoms of H. The bond energy of H—Cl can be calculated as the arithmatic or geometric mean of the two bond energies of Cl—Cl and H—H. In the same way, calculations for bond energies of other molecules can be derived. Bond energies of molecules can also be directly determined experimentally. The difference between the calculated bond energies and the experimentally determined values, Δ, is a measure of the polarity of the bond and is related to the electronegativity. The greater the difference in bond energies, the greater is the polarity and hence greater will be the difference in electronegativity values of the atoms forming the molecule. These facts are illustrated in Table 3.11 with some examples.

Table 3.11. Bond energy and electronegativity difference.

Bond *A—B*	*Calculated mean bond energy Kcal / mole*	*Experimental bond energy Kcal / mole*	*Energy difference* Δ	*Electronegativity difference between A—B*
Si—F	43	128	85	2.2
H—F	67	135	68	1.9
H—O	59	108	49	1.4
H—Cl	79	103	24	0.9
Cl—O	43	49	6	0.5

QUESTIONS AND PROBLEMS

1. Explain how positive and negative ions are formed from neutral elements.
2. What is meant by "ionization potential"? How is it related to the tendency of the elements to form positive or negative ions?
3. Explain the term "electronegativity" of the elements.
4. What is meant by polar molecule ? Give example.
5. How the polarity of bond in a molecule is related to electronegativity differences between the atoms of the molecules?
6. Explain Fajans' Rule with examples.
7. Discuss : (a) The ionic character of covalent bond, (b) The covalent character of ionic bond.
8. What is meant by radius-ratio effect in ionic crystals? How it governs the geometrical shape of the crystalline substances?
9. Define the following :— (a) Crystal lattice (b) Lattice energy, (c) Crystal co-ordination number, (d) Polarisation, (e) Electron affinity, (f) Bond length, (g) Bond angle, (h) Bond energy, (i) Covalent radii, (j) Ionic radii.
10. Which of the following pairs of substances should be more polar than the other? (a) H_2O and H_2S; (b) HI and HF; (c) AlF_3 and $AlCl_3$; (d) KCl and PCl_3; (e) ICI and KI.
11. Discuss the bonding systems and shapes of the following molecules : NH_3 ; SF_4; PCl_5; $SiCl_4$
12. The bond lengths of Cl_2 and Br_2 are 1.988 Å and 2·290 Å respectively. Find the length of the Br–Cl bond in bromine monochloride.
13. Given H to H distance in NH_3 is 0.1634 nm and N–H bond distance is 0.101 nm. Calculate the bond angle H–N–H.
14. The electronegativities of F, Cl, Br and I are 4.0, 3.0, 2.8 and 2.5 respectively. Explain why the dipole moments decreases in the sequence HF, HCl, H Br. and HI, even though the bond length and the number of electrons increase.
15. Bond evergies for the following bonds are :

    H—H = 104 Kcal/mole

    O = O = 118 ,,

    O = H = 111 ,,

    Calculate energy change in the reaction :

    $2H_2(g) + O_2(g) = 2H_2O(g)$.
16. Calculate the heat of formation ΔHf of crystalline NaF using the following data according to Born-Haber cycle.

$Na(g)$	$\rightarrow$	$Na(g)$	= + 26.0 Kcal (S)
$F_2(g)$	$\rightarrow$	$2F(g)$	= + 36.6 Kcal (D)
$Na(g)$	$\rightarrow$	$Na^+(g)$	= + 120.0 Kcal (I)
$F(g) + e^-$	$\rightarrow$	$F^-(g)$	= – 83.5 Kcal (E)
$Na^+(g) + F^-(g)$	$\rightarrow$	$Na^+F^-(s)$	= – 216.7 Kcal (U)

CHAPTER 4

CLASSIFICATION OF THE ELEMENTS

The 105 substances well-known as elements are the foundation of the study of chemistry. Attempts have always been made to discover an arrangement and order in a complex science such as chemistry comprising a vast number of experimental facts about all the 105 elements. In order to facilitate a systematic study of the vast facts we must classify them in a way that lays emphasis on similarities and differences between isolated and unrelated phenomena. The earlier attempts at such a classification have been attributed to many scientists and proved to be very useful in developing the modern system which is based upon the electronic arrangement of atoms. It is, therefore, worthwhile to trace the developments.

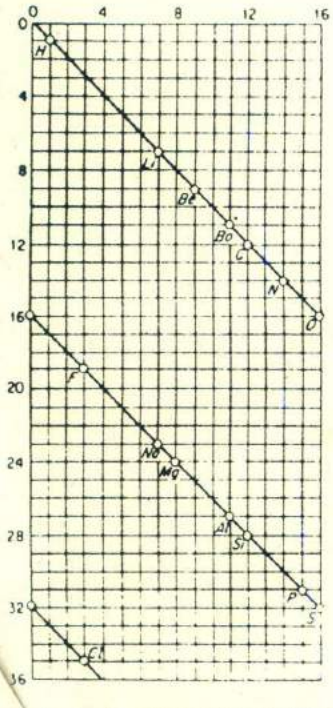
Early Attempts at Classification

1. Noble Metals and Base Metals : In one of the earliest attempts at the classification, the metals were divided into two groups. gold and silver were considered to be noble metals, whereas copper, iron, tin lead etc. were included among the base metals. When elements which are non-metals were discovered, a further classification into metals and non-metals were introduced and made it possible to anticipate the difference in the properties of hitherto unknown elements.

2. Dobereiner's Triads : In 1829, J. W. Dobereiner observed that several of the elements could be grouped together in sets of three, called *triads*, which have closely related properties. The triads are found to have either nearly the same atomic weights or differ by an almost constant difference. Using present-day atomic weights which are more accurate than those used by Dobereiner, the relationships among some triads may be shown as in Table 4.1.

Table 4.1 Dobereiner's Triads.

Triads	*Atomic weights*	*Difference between consecutive elements*
Li	6.940	
Na	22.997	16.057
K	39.100	16.103
Cl	35.457	
Br	79.916	44.459
I	126.91	46.994
Fe	55.85	
Co	58.94	Almost the same at. wts.
Ni	58.71	



4—1. A portion of the Telluric Screw on a flat surface

The triads of Dobereiner represent the first reported attempt at classification of elements on the basis of atomic weights. This observation stimulated further attempts to seek additional and wider numerical relationships. But most of the attempts did not meet with much success, largely because the atomic weights were not evaluated correctly. Mention may be made about Pettenkofer series which suggested that the atomic weights of chemically similar elements can be represented by arithmatic series. Thus oxygen, sulphur, selenium and tellurium could be classed as family of elements represented by the series $1+2n\times8$ where $1=$ at. wt. of O and $n=0, 1, 2, 3$, A French scientist, de Chancourtois, constructed a vertical cylinder on which he arranged the elements spirally at heights proportional to their atomic weights. It was found that

similar elements appeared above one another on the cylinder. This arrangements is known as the Telluric Screw and this proved to be the forerunner of the modern classification of elements. A flat surface of the Telluric Screw is shown in Fig. 4—1.

3. Law of Octaves : In 1864, John Newlands arranged the elements in the increasing order of their atomic weights and observed that every eighth element in the list beginning from any given element showed a repetition of the physical and chemical properties of the first element. Because of its resemblance with the eight notes in musical scale this concept of the classification of elements was known as the Law of Octaves. Unfortunately this basically sound idea was not well received by scientists of Newlands' time. It may be pointed out that the inert gases were not then known and the discovery of the inert gases completely shelved the idea of the Law of Octaves.

Periodic Law :

In 1869, a German chemist, Lothar Meyer, and a Russian scientist, Dmitri Mendeleeff, working independently and from different viewpoints, proposed a detailed relationship between the physical and chemical properties of the

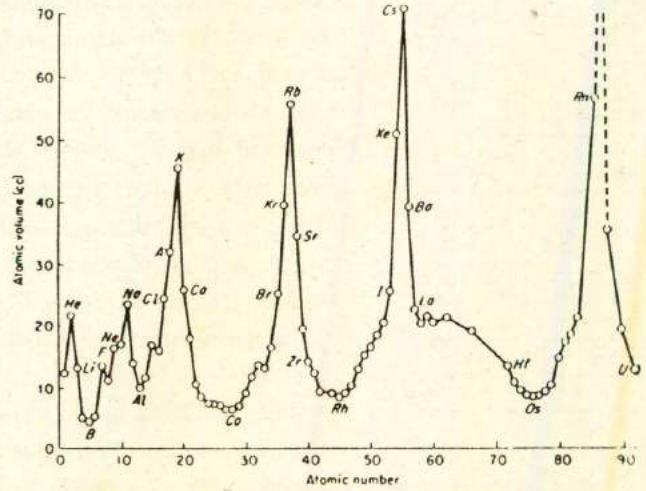


Fig. 4—2. The atomic volume curve of the elements.

elements and their atomic weights. Meyer selected some physical properties related to the atomic weights, namely atomic volume. Taking atomic numbers instead of atomic weights as the basis a graph of atomic volumes (the volume occupied by 1 g. atom of an element or at. wt. divided by the density) against atomic numbers is shown in Fig. 4—2. This graph does reveal a periodic variation of atomic volume when the elements are arranged in the increasing order of atomic weights or atomic numbers. It may be noted that a periodic variation repeats itself more or less at regular intervals or periods with the change of variables. Thus the change of seasons in a year is a periodic phenomenon. Night and day are periodic phenomena. The swing of a pendulum to and fro is a periodic phenomenon.

Mendeleeff gave a more detailed comparison of the physical and chemical properties of the elements and set up a periodic system in which the elements were arranged in horizontal ROWS (series) and vertical COLUMNS (groups) according to increasing atomic weights. This arrangement is the basis of our modern Periodic Table. Mendeleeff observed that when all the 65 elements (known at that time) were arranged according to increasing atomic weights, similarities and differences in their properties would be apparent. This was enunciated in the form of a PERIODIC LAW which stated that the physical and chemical properties of the elements are periodic functions of their atomic weights.

The discovery of rare gases during 1890—1900 did not produce any serious difficulty with regard to Mendeleeff's PERIODIC TABLE. Mendeleeff is usually given the principal credit for establishing the periodic system of the elements.

With the advancement of our knowledge about atomic structure and discovery of new elements, a modification in the definition of periodic law was proposed on the basis of atomic number. The modern statement of the periodic law is:

The physical and the chemical properties of the elements are periodic function of their atomic numbers.

There are various forms of the Periodic Table and a modern long form is given in Table 4.2. based on Aufbau Principle (building up of the atomic electronic configurations. As the nuclear charge increases, the electronic configurations become more complex.

The Modern Periodic Table

The original Periodic Table suggested by Mendeleeff has undergone many modifications, although the basic features have been maintained in all the modified forms.

It is seen that the first short period (horizontal series) contains only two elements—hydrogen and helium. Helium has a complete energy level of two electrons ($1s^2$). The second short period consists of eight elements beginning with lithium and ending with neon. Neon has complete electronic arrangements of $1s^2 2s^2 2p^6$ and contains 8 electrons in the outermost level. The third short period again consists of eight elements beginning with sodium and ending with argon. Argon has the electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$ and the outermost energy level contains 8 electrons.

The fourth period is the first long period containing eighteen elements and this period starts from potassium (atomic number 19). Potassium has electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ and the next element calcium (atomic number 20) has one more election in 4s level, i. e., $4s^2$ and thereby making it complete. Scandium having atomic number 21 with the electronic arrangements $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$ starts building up the 3d energy level. The process of filling up of 3d level is completed until copper (atomic number 29). In copper the third quantum level contains 18 electrons. Each succeeding element in this period contains one more electron in the fourth quantum level. The fourth period comes to an end with the inert gas krypton (atomic number 36) containing eight electrons in the outermost energy level.

The fifth period begins with rubidium (atomic number 37). The last element is xenon (atomic number 54) and contains again eight electrons in the outermost energy level. The process of filling up of the energy levels follows the same pattern as in the fourth period and, therefore, the fifth period also contains eighteen electrons.

The sixth period consists of thirtytwo elements. This period starts from cesium (atomic number 55) having one electron in the 6s level, i.e., $6s^1$. The next element barium has two electrons in the 6s level. the next fifteen elements starting from lanthanum (atomic number 57) to lutecium (atomic number 71) contains 8 and 2, or 9 and 2 electrons respectively in the two outermost energy

levels together with increasing number of electrons in the inner **4f** orbital. The fourteen elements starting from Ce (58) to Lu (71) have almost identical chemical properties and all are placed in the same position in the Periodic Table. They are known as rare earth elements and constitute the lanthanide series named after lanthanum. From cerium to lutecium each succeeding element has one more electron in the **4f** energy level. Lutecium (atomic number 71) and above have a total of 32 electrons in the fourth energy level. The single electron in the **5d** energy level in all the elements from lanthanum to lutecium starts building up with hafnium (atomic number 72) and becomes complete ($5d^{10}$) in gold (atomic number 79). From gold to the end of the period each such succeeding element has one more electron in the **6p** energy level. The period ends with the inert gas radon (atomic number 86) containing 8 electrons in the outermost energy level ($6s^26p^6$). The seventh period is still incomplete. The first element francium (atomic number 87) has one electron in **7s** energy level and after radium (atomic number 88) with $7s^2$ electrons the building up of **6d** level starts but for all the elements upto the present element hahnium (atomic number 105) it remains constant, i.e., consists of only one electron. From actinium (atomic number 89) a new series of elements starts which is known as actinides and may be considered to be complete at the element having atomic number 103 (Lr) placed along with lanthanides below the Periodic Table.

The elements actinium, thornium, protoactinium and uranium are naturally occurring radioactive elements in the actinide series. The eleven elements after uranium, known as transuranium elements, have been made artificially. Because of the filling up of the **5f** energy level and identical electron arrangements in the **6d** and **7s** energy levels, the actinide series of elements have similar chemical properties. Like the lanthanides these are also placed in one position after radium in the Periodic Table. The recently discovered element kurchatovium (atomic number 104) is the beginning of the seventh period which is incomplete and will be considered to be complete at the element of atomic number 118. The next element (atomic number 105) has been named tentatively as hahnium (Ha).

The vertical arrangements of elements in the Periodic Table are called ıps. It may be seen that the groups are numbered IA, IIA IIIB, IVB VB, VIB, VIII, IB, IIB, IIIA, IVA, VA, VIA, VIIA and 0. The elements in sub-

group A show some similarities to the corresponding elements in the B sub-group of the same number. The sub-grouping of elements was originally empirical, but now it is based on the electronic arrangement of the atoms. The division into the sub-groups A and B is based on the fact that the penultimate energy levels (last but one quantum level) of electron in these groups contain the arrangement s^2p^6 and $s^2p^6d^{10}$ respectively. It may be noticed that the similarities between A and B sub-groups of the same group of elements sometimes are confined only in the oxidation states and some of their compounds. Thus manganese in group VIIB is a metal and chlorine in VIIA is a non-metal and a gas. However, oxidation states of +7 for Mn in $KMnO_4$ and Cl in $KClO_4$ is common for both and these compounds have similar crystalline form, solubility and oxidizing action.

The elements in group VIII have no sub-groups, instead these consist of three elements in one single group of the Periodic Table and occur in the middle of each long period. These have striking horizontal similarities. This group contains iron, cobalt and nickel in the fourth period' ruthenium, rhodium and palladium in the fifth period; and osmium, iridium and platinum in the sixth long period. The group VIII elements may be called bridge elements, because they form bridge between the hard, high melting metals of group VIB and VIIB and the softer metals of group IB and IIB. The inert gases, having elements of completed electronic levels, are placed at the end of the period where they fit excellently and are termed as elements of group 0.

Electronic Structure and the Periodic Law

Types of Elements : According to the electronic configurations, the elements may be divided into four types. Mention has already been made regarding the four types of atoms on the basis of electronic arrangement. The four types of elements are :

(1) The Inert Gases. (Elements of 0 group).

(2) The Representative Elements (s and p book elements).

(3) The Transition Elements (d block elements).

(4) The Inner Transition Elements (f block elements)

The Inert Gases : The zero group elements have been placed at the end of each period in the Periodic Table. It appears that these elements having s^2p^6 electronic arrangements in the outermost level are very stable. Helium has $2s^2$ stable arrangement and all other inert gases have s^2p^6 outer configurations. It may be noted that no atom has a complete energy level except helium and neon. This is one reason that discontinuities in the building up of energy level take place. These elements are colourless gases.

The Representative Elements (s and p block elements) : These elements generally belong to A sub-group of the Periodic Table.These elements have the outermost energy level incomplete just after the complete or stable groupings of s^2p^6. The chemical behaviour of these elements depends upon the valence electrons and these are both metals and non-metals. Thus the alkali metals, alkaline earth metals are **s** block or **s** orbital elements. Group IIIA elements under boron have a single electron in their valence **p** orbitals. The valence electrons of all the elements from boron to halogens (groups IIIA to VIIA vertically) occupy **p** orbitals. Hence these elements are called **p** block or **p** orbital elements. They generally form colourless compounds.

The Transition Elements (d block elements) : These elements are generally heavy metals of sub-group B and contain two incomplete energy levels because of the building up of the inner **d** electrons. The chemical properties of these elements depend upon the electrons from the two outermost levels (**s** and **d** electrons). These elements generally form coloured compounds.

As the atomic number increases each successive electrons enters the outermost energy level of the atom. But sometimes the additional electron enters one of the inner levels, such as the 3**d** on account of its lower energy than 4**p**, although this is not attained until 4**s** levels is completed. When 4**s** has got its 2 electrons, the next electron now goes to 3**d** instead of 4**p** and as the atomic number increases, it is the 3**d** level which is being filled up. The 4**s** continue to have 2 electrons and the properties of the successive elements do not appear to change much. Elements which have normally the same number of electrons in the outermost level but have a progressively greater number of electrons in an inner level (such as **d** level) are called "Transition Elements". In the Periodic

Table 4.2. The Periodic Table of elements(Long form).

Period ⟶
s block elements
Group ↓ IA IIA

p block elements

d block elements

Transition elements

s electrons

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	O
H 1																	He 2
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12											B 13	C 14	N 15	O 16	F 17	Ne 18
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La 57	Hf 58	Ta 59	W 60	Re 61	Os 62	Ir 63	Pt 64	Au 65	Hg 66	Tl 67	Pb 68	Bi 69	Po 70	At 71	Rn 72
Fr 87	Ra 88	Ac 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	(110)	(111)	(112)	(113)	(114)	(115)	(117)	(118)	(119)
(119)	(120)	(121)	(154)	(155)	(156)	(157)	(158)	(159)	(160)	(161)	(162)	(163)	(164)	(165)	(166)	(167)	(168)

Lanthanides	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
Actinides	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103
Superactinides	(122)	(123)	(124)											(153)

Table we come across four such transition series in which the additional electrons enter the 3d, 4d, 5d and 6d orbitals. some of these are shown in Table 4.3.

Besides the transition elements, there are the inner transition elements in which not only the d levels but also the 4f or 5f levels are being progressively

Table 4.3. Outer electron levels of the transition metal groups.

21	Sc	$3d^14s^2$	39	Y	$4d^15s^2$	57	La	$5d^16s^2$
22	Ti	$3d^24s^2$	40	Zr	$4d^25s^2$	72	Hf	$5d^26s^2$
23	V	$3d^34s^2$	41	Nb	$4d^45s^1$	73	Ta	$5d^36s^2$
24	Cr	$3d^54s^1$	42	Mo	$4d^55s^1$	74	W	$5d^46s^2$
25	Mn	$3d^54s^2$	43	Tc	$4d^55s^2$	75	Re	$5d^56s^2$
26	Fe	$3d^64s^2$	44	Ru	$4d^75s^1$	76	Os	$5d^66s^2$
27	Co	$3d^74s^2$	45	Rh	$4d^85s^1$	77	Ir	$5d^76s^2$
28	Ni	$3d^84s^2$	46	Pd	$4d^{10}$	78	Pt	$5d^96s^1$
29	Cu	$3d^{10}4s^1$	47	Ag	$4d^{10}5s^1$	79	Au	$5d^{10}6s^1$
30	Zn	$3d^{10}4s^2$	48	Cd	$4d^{10}5s^2$	80	Hg	$5d^{10}6s^2$

filled up. These are generally called the Lanthanides (the rare earths) and the Actinides (mainly trans-uranium elements).

The first transition series of elements involving the completion of 3d level start from Sc (21) to Zn (30) which may be discussed as the elements of representative characters. The second series of transition elements start from Y (39) upto Cd (48) involving 4d energy level. The third group of transition metals starts from La (57) but with a break from Ce (58) to Lu (71) which are classified as inner transition metals and proceed upto Hg (80). Sometimes the metals of group IIB, namely, Zn, Cd, Hg, are not included in the transition metals. But for the sake of systematic study of chemistry they are included as transition metals on the basis of electron arrangement.

The properties of transition elements are summarized in the following points :—

1. All the elements are of high melting points, electropositive and heavy metals.
2. These metals have almost the same atomic and ionic sizes. There is only slight increase in the ionization energy of the formation of M^{+2} ions.
3. All these elements show positive oxidation states of +2 and +3 generally and form mostly ionic compounds. Higher oxidation states are also exhibited in some cases.
4. As a general rule, the transition elements form coloured compounds.
5. These elements are also effective catalytic agents.
6. All these form quite a large number of complex compounds.

These properties are due to the influence of the incomplete inner **d** orbitals in the transition elements. The properties are similar in the case of inner transition elements where **f** orbitals are being completed (see Chapter 18).

The Inner Transition Elements (f block elements) : These elements have three incomplete outer levels. The orbital in which the electron is added on increasing the atomic number is an **f** orbital. The series of 14 elements in which 4**f** level is being build up follows lanthanum (57) and are called Lanthanides. The series of elements in which 5**f** level is being filled follows actimium and is known as Actinides. The inner transition elements (lanthanides and actinides) are all metals and show variable oxidation states. Their compounds are highly coloured (see Chapter 18). Lawrencium (103) is the last element of the actinide series. The recently discovered element now named Rutherfordium (104) is, therefore, the first element of the Transactinide series and should be chemically similar to lanthanum and hafnium. The report of the discovery of element 105 (Hahnium) now named as Dubnium by the Russian scientists and if the synthesis of the new elements continues, it is expected that elements 114 and 126 should possess increased stability. The most suitable means to achieve such a break-through towards the farther reaches of Periodic Table is evidently the bombardment of heavy nuclei. This requires more powerful cyclotrons and possibly a *superactinide* series of elements may be discovered. (see page 138 and 154)

Periodicity of Valence Electrons : When the elements are arranged in order of increasing atomic numbers, elements with similar physical and chemical

properties repeat at definite intervals. In regard to atomic structure, it implies a periodicity in the number of valence electrons in the atoms of elements. If the elements containing the same number of valence electrons are grouped together, the elements within each group will be similar in properties. Table 4.4 gives the electron levels for the elements of atomic numbers in the beginning of the Periodic Table showing the periodicity as regards the number of electrons in the outermost energy level.

Table 4.4 Periodicity of valence electrons.

Element	H							He
Electron level	1							2
Element	Li	Be	B	C	N	O	F	Ne
Electron level	2,1	2,2	2,3	2,4	2,5	2,6	2,7	2,8
Element	Na	Mg	Al	Si	P	S	Cl	Ar
Electron level	2,8,1	2,8,2	2,8,3	2,8,4	2,8,5	2,8,6	2,8,7	2,8,8

It is seen that the elements in the vertical columns (groups) have the same number of electrons in the outermost energy level. The similarity in the chemical properties among the elements of the same group can be attributed to the number of electrons in the outermost energy level of an atom. Periodicity as regards valence electrons is reflected in the periodicity of oxidation states (the number of positive or negative charges of the atoms). This feature is shown in Table 4.5.

Table 4.5. Periodicity of Oxidation State.

+1 H							0 He
+1 Li	+2 Be	+3 B	+4,–4 C	+5,–3 N	–2 O	–1 F	0 Ne
+1 Na	+2 Mg	+3 Al	+4,–4 Si	+5,–3 P	–2 S	–1 Cl	0 Ar

Hydrogen, lithium and sodium have one valence electron each, and each shows an oxidation state of +1 when this electron is transferred to another atom in the formation of chemical bonds. Carbon and silicon atoms with four valence

electrons may form four polar covalent bonds in which the shared electron pairs are shifted away (+4 oxidation state) or move towards (–4) oxidation state) of the carbon or silicon atom. Fluorine and chlorine atoms, each with seven valence electrons, normally assume completed octets by the addition of one electron giving them–1 oxidation states.

Variation of Properties within Periods and Groups

The physical and chemical properties of the elements are largely determined by their electronic structure. Differences in the properties within groups may be attributed primarily to three characteristics of atomic structures : (i) The nuclear charge and the number of electrons surrounding the nucleus (atomic number). (ii) The total number of electrons—particularly the number of valence electrons. (iii) The size of the atoms, i.e., the volume occupied by the electron in various energy levels.

1. Variation of Metallic Character of the Elements : Generally, it may be noticed that in the Periodic Table the metallic character of the elements decreases from left to right progressing in the series but increases in moving vertically from top to bottom in the groups.The term "metallic character" is a rough and qualitative combination of a number of specific properties, such as electrical and thermal conductivities, metallic lustre, reducing properties etc. Except the transition elements, the trend in the variation of metallic character of elements follows the above generalisation. For instance, the most non-metallic elements, fluorine, chlorine, oxygen, sulphur, nitrogen are found at the upper right of the Periodic Table whereas the most basic matals, the alkali and alkaline earth metals are at the lower left of the Table.

2. Variation in Atomic Size : The atomic size in each succeeding element in a period decreases but the atomic radii of inert gases at the end of the periods, however, are larger than those of the elements of the preceding atomic number. The inert gases have completed outer energy levels, i. e., the **p** sub-level has been filled up with six electrons (p^6). As the nuclear charge increases in a period the electrons may occupy the same or different energy levels. When the succeeding electrons go into the same energy levels they are subject to greater attraction by the increased nuclear charge and hence the elements in a series show gradual decrease in the atomic size. Since the inert gases, such as

argon, exhibit very weak binding force to hold the atoms together in a crystal lattice, the interatomic distances and atomic radii of these elements become greater than those of the preceding halogens.

The gradation from highly metallic sodium to highly non-metallic chlorine in the third period shown in Table 4.2 is explainable in terms of the smaller size of each succeeding element in the series. The tendency for each succeeding element to become less metallic results from the fact that the valence electrons are less readily lost as their distance from the nucleus becomes less, and the attraction for additional electrons from other atoms becomes greater.

Vertically in the groups the succeeding elements have increasing atomic radii. Thus, each alkali matal atom has a much greater atomic radius than that of the inert gas just before it. This is due to the fact that the additional electron occupies a new sub-level with a quantum number higher than those of the already filled energy levels. These elements become more metallic, i.e., lose valence electrons more readily as their size increases. This results from the fact that the valence electrons are held less strongly due to the increasing size of the atom.

A similar trend is noticed in the long periods but the gradation is less marked and also shows some exceptions, such as in Rh—1.24Å, Pd—1.28Å, Ag—1.34Å. Within a given group the heavier elements have the larger atomic size.

3. Variation in Ionic Radii : It is obvious that the size of a positive ion will be less than that of the atom from which it is formed. There is considerable decrease in size due to the loss of the outermost electron particularly in the case of alkali metals. In the cases of ions having inert gas electronic configurations, the contraction in size in a given period is well-marked. Thus in the series, Na^{+}, Mg^{+2}, Al^{+3} and Si^{+4}, which are isoelectronic with argon configuration, the decrease in their ionic sizes appears to be considerable as compared to the atomic sizes of the parent atoms. It will be seen that greater the nuclear charge, the smaller is the ionic radius in a series of isoelectronic ions. In a given group of the Periodic Table positive ions of succeeding elements have larger ionic radii.

A simple negative ion formed by the addition of one or more electrons to the outermost energy level of an atom, is expected to be much larger than the

parent atom. In a given group the negative ions will have larger radii due to larger number of electron levels. The ionic sizes in a series also follow the same trend as in the case of the positive ions, i.e., the sizes decrease gradually from element to element. The trends are given in the Table 4.6 and Table 4.7.

Table 4.6. Trend in ionic sizes in a series.

Atom	Na	Mg	Al	Si	P	S	Cl	Ar
Radius(Å)	1.86	1.60	1.48	1.17	1.10	1.04	0.99	1.54
Ion	Na^+	Mg^{+2}	Al^{+3}	Si^{+4}	P^{-3}	S^{-2}	Cl^-	Ar
Radius(Å)	0.95	0.78	0.57	0.40	2.12	1.84	1.81	1.54

Table 4.7 : Trends in ionic sizes in a group(Å)

Atom	*Radius*	*Ion*	*Radius*
Li	1.52	Li^+	0.60
Na	1.86	Na^+	0.95
K	2.31	K^+	1.33
Rb	2.44	Rb^+	1.48
Cs	2.62	Cs^+	1.69
F	0.72	F^-	1.36
Cl	0.99	Cl^-	1.81
Br	1.14	Br^-	1.95
I	1.33	I^-	2.16

In the Long Periods, the ionic sizes of transition metals of the same charge (say, M^{+3}) show slight gradation with irregularities. The radii of the rare earth ions (M^{+3}) show regular decrease from lanthanum to lutecium. It is due to the relationship between ionic sizes and chemical properties that the pairs of elements, such as Zr and Hf, Nb and Ta, Mo and W, have almost identical chemical behaviour. These pairs of elements although placed widely apart in the

Periodic Table have almost identical ionic radii due to the trends in the variation of ionic sizes.

4. Variation in the Ionization Potentials : Ionization potential of an atom is the most important fundamental property of an atom and the metallic character is largely determined by its ionization potential, its atomic radius and its ionic radius. These three properties may be interdependent since the ionization potential is defined as the energy required to remove the outermost electron from an atom. In general, the greater the nuclear charge of atoms having the same number of electron orbit, the greater the ionization potential. Thus the elements in the same period have gradually increasing ionization potential. Slight irregularity within a period is due to building up of new sub-level for electrons. Metals generally have small ionization potentials and non-metals have large values. This indicates that metals give positive ions readily by the loss of electron and non-metals have no tendency to form positive ions during chemical reactions. The magnitude of the ionization potential to some extent gives a measure of the chemical activity of an element (particularly of metals). Thus the ionization potential increases in a series and shows decreasing tendency with a group in the periodic classification. In other words, the periodic variations are well-marked (see Fig. 3—1. page 111)

5. Variation in Electron Affinities : Electron affinity, as defined earlier, is a measure of the energy released when an electron is added to an atom to form a negative ion. Metals obviously have small electron affinities and non-metals, on the other hand, have large values of electron affinities and are therefore, good oxidising agents. In general, in a series of elements of a given period of the Periodic Table succeeding elements have higher electron affinities. Within a group having smaller electron affinities the metallic character becomes more prominent.

6. Variation in Electronegativities : The power of attraction that an atom shows for electron in a covalent bond (electronegativity) also shows periodic variations. The most electronegative elements are found towards the end of the periods. Metals having low electronegativities are found at the beginning of the periods. Thus the alkali metals show gradually decreasing electronegativity

values within the group. The halogens are most electronegative elements and the values decrease from fluorine to iodine. It follows that elements at the extreme left of the Periodic Table form ionic bonds with, say, halogens. The elements adjacent to one another in a period generally form covalent bonds. The variations of electronegativities with the atomic numbers of elements are given in Fig. 4—3.

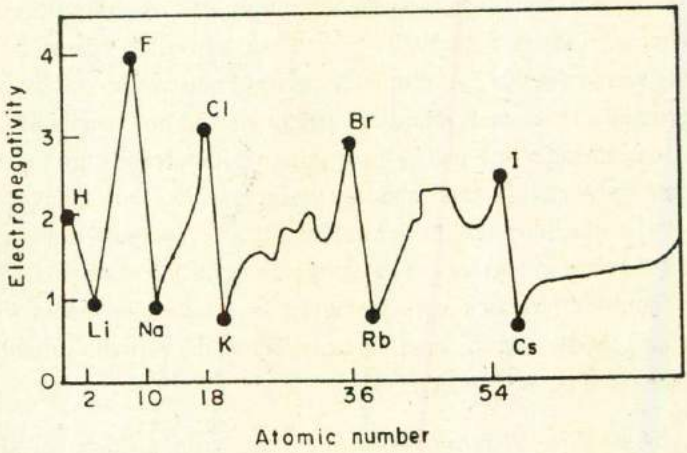


Fig. 4—3. Variation of electronegativities with atomic number of elements.

Table 4.8. Variation in electronegativities of some elements in series and groups.

Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na						Cl
0.9						3.0
K						Br
0.8						2.8
Rb						I
0.8						2.4
Cs						
0.7						

7. Variation in the Stability of Oxidation States :The transition elements generally exhibit more than one oxidation states. This is due to successive loss of electrons from the inner partially filled d sub-level. Thus, vanadium shows +3, +4 and +5 states and for chromium +2, +3 and +6. Those for manganese are +2, +3, +4, +6 and +7. It may be noted that the higher oxidation states become more stable near the bottom of each transition metal groups in the Periodic Table whereas the stability of +3 state decreases in the opposite order.

Among the families of post-transition metals having completely filled d levels if there are two possible oxidation states, it is found that the lower one is more stable than the higher ones. Thus in the case of tin having the electron configuration :

Sn	...	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$3d^{10}$	$4s^2$	$4p^6$	$5s^2$	$4d^{10}$ $5p^2$
Sn^{+4}	...	...	...	...	...	...	...				$4d^{10}$ ($5s^2$ and $5p^2$ lost)
Sn^{+2}	...	...	...	...	...	...	...				$5s^2 4d^{10}$ ($5p^2$ lost)

$5s^2$ electrons in Sn occur after $4s^2\ 4p^6\ 4d^{10}$ completed levels and are inert in Sn^{+2}.

The inner $5s^2$ electrons are more inert and are referred to as "inert pair" of electrons. Hence Sn^{+2} is more stable than Sn^{+4}.

8. Variation in the Oxidising and Reducing Powers : Oxidising substances have tendency to accept electrons and are converted into lower oxidation states. The non-metals at the extreme right of the Periodic Table having high ionization potentials, electron affinities and eectronegativities tend to act as oxidising agents in chemical reactions with other substances. Similarly, reducing substances give up electrons and are converted into higher oxidation states during chemical reaction. The reducing power is the highest with the metals at the beginning of the periods, where the ionization potentials, electron affinities and electronegativities are low. Thus, alkali metals have the greatest reducing power. In general, the reducing power of the elements is progressively lower as we pass across the periods and higher, as we go down the groups. Francium should be the strongest reducing agent and fluorine, the strongest oxidising agent of all the elements.

9. Variation in the Basic Properties : The hydroxides of elements at the beginning of the Periodic Table dissociate in water solution giving OH-ions and show basic characters. The large positive ions form hydroxides which are strongly basic. On the other hand, elements of small positive ions at the end of the periods form hydroxides which in water give acidic behaviour. In general, the metals on the left of the Periodic Table form basic oxides and the non-metals on the right form acidic oxides. This accounts for the fact that the positive ions may exist in water solution with hydroxide ions (OH^-) and the negative ions may be found in water solution with a high concentration of hydronium ions (H_3O^+).

When an element exhibits two or more oxidation states, the ion of the element in its lowest state is less electronegative than in the higher state and the lowest state is the more basic than the higher one. Thus stannous ion is more basic than stannic ion.

10. Variation in Physical Properties : Almost any physical property of the elements, when plotted against the atomic numbers, shows periodicity and the curves obtained have remarkable similarity with the atomic volume curve. Thus the densities of the elements in the solid state vary periodically with their atomic numbers. The variation occurs in a regular manner within a period and shows a maximum in the central members.

Similarly, melting points and boilding points show periodic vaiations. The inert gases show minimum melting points and boiling points and occur at the bottom of the melting point curve against atomic number. The elements of groups IV and VI occupy the peaks as shown in Fig. 4—4.

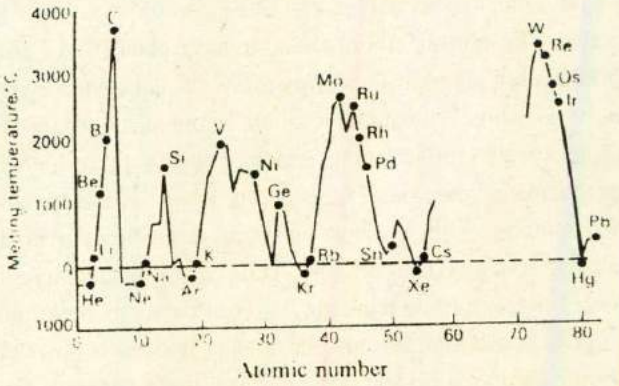


Fig. 4—4. Periodicity of melting points.

Many other physical properties such as hardness, malleability, compressibility, coefficient of expansion, thermal conductivity and electrical resistance likewise show periodic variations.

Borderline elements mostly in the middle region of the Periodic Table exhibit both metallic and non-metallic properties and are known as metalloids. They usually act as electron donors with non-metals, and as electron acceptors with metals. It is not very well-defined as to which elements should be included in this class. But they generally occur near about the middle of the Periodic Table. Such elements are boron, silicon, germanium, tellurium etc. They are all solids at room temperature, somewhat brittle and poor conductors of heat and electricity.

Usefulness of the Periodic Table

The systematic arrangement of the elements found in the Periodic Table has greatly simplified the task of organising the extensive mass of knowledge relating to the chemistry of the elements as a whole. The following important applications of the Periodic Table may be mentioned :—

1. Classification of the Elements : The classification of elements of similar properties into groups simplified their study. For instance, sodium, a member of the alkali metals group reacts with water vigorously giving hydrogen gas and forming sodium hydroxide which is a strong base. The other alkali metals, lithium, potassium, rubidium, cesium and francium also react with water in a similar manner. Halogens, again, show properties which are all alike.

It may be noted that similarities of properties in a group actually show gradation. In some cases this gradation is very well-marked.

2. Prediction of Undiscovered Elements : At present all the elements from atomic number 1 to 105 have been discovered and their properties are more or less known. But a very remarkable use of the Periodic Table was made by Mendeleeff in predicting a number of undiscovered elements which were shown by a number of gaps in the then Periodic Table. It may be remembered that Mendeleeff's Table contained only 65 elements with a large number of vacant places. Mendeleeff predicted the existence and properties of 6 elements corresponding to the gaps. These elements have since been discovered and are

scandium, gallium, germanium, technetium, rhenium and polonium. It is surprising that these elements have properties quite similar to those predicted by Mendeleeff.

Elements having atomic number 43, 61,85 and 87 were also missing from the Mendeleef's Table and discovered later.

3. Correction of Atomic Weight : Atomic weights of some of the elements at the time of Mendeleeff gave a wrong position to some of the elements in the Periodic Table. The properties of these elements required their placement somewhere else. These discrepancies have been a matter of great research by chemists and physicists. For instance, the element 'indium' was placed in a vacant place in the Periodic Table between Cd (112.4) and Sn (118.7) and indium with atomic weight of about 114 fitted very well in between Cd and Sn.

4. Periodic Table in Industrial Research : The Periodic Table has been found to be quite useful in industrial researches. Several of the light metals and their alloys used in modern mechanical equipments, jet engines and air-crafts were first studied in detail because of their position in the Periodic Table. The search for tetraethyl lead as an anti-knock compound to be added to modern ethyl gasoline, was found as the result of great need for such materials by looking through the Periodic Table for elements having such properties. Another classical example of the application of the Periodic Table to an industrial problem was in connection with the development of Freon, a non-toxic, non-inflammable refrigerant. It is easily visualized by a look at the Periodic Table that compounds of the non-metallic elements in the upper right-hand region of the table are volatile enough to act as refrigerant. Thus, fluorine compounds would possess such properties and as a result Freon, CF_2Cl_2, was discovered.

Limitation of the Periodic Table

There are certain inherent weakness in the Periodic Table although it has been immensely successful in producing a systematic classification of chemical knowledge.

1. Position of Hydrogen : The position of hydrogen in the periodic table is left undecided. It has similarities in properties with both the alkali

metals and the halogens. According to the atomic number or atomic weight, hydrogen should occupy a position just before helium.

Hydrogen is a gas like fluorine and chlorine and forms compounds like CH_4, SiH_4 which are like CCl_4 and $SiCl_4$ respectively. Even solid hydrogen is a non-metal resembling iodine. The hydrogen molecule is diatomic like halogen.

On the other hand, hydrogen resembles lithium and other alkali metals in having one electron $1s^1$ which can be lost in forming the hydrogen ion. Under most conditions, however, hydrogen does not lose this electron, but shares it with other atoms. Again, sodium hydride and sodium fluoride are both crystalline ionic solids, a point which shows similarity of hydrogen with fluorine. But in most cases it assumes a +1 oxidation state. For this reason, hydrogen is usually included in group IA of the table. Actually, hydrogen shows no relationship with any other element.

2. Anomalies in the Mendeleeff's Table : When the atomic weights of the elements were adopted as a basis for periodic classification, a number of anomalies were observed with regard to the placement of some elements of similar properties. Thus potassium (39.1) should come before argon (39.94). Similarly, tellurium (127.5) comes before iodine (126.93) and cobalt (58.4) should be placed after nickel (55.69). These anomalies disapeared automatically when atomic number was adopted as the basis of periodic classification and these elements occupy positions justified by their atomic numbers.

3. The Position of Rare Earths : The rare earths are also known as lanthanides. These elements have the two outermost energy levels identically occupied by electrons which give them great similarity in properties. All of them are metals. Their compounds are very closely related to one another which involved tremendous difficulties in their separation. All these elements are, therefore, placed in one and the same group. Starting from lanthanum (57) to lutecium (71), these fifteen elements actually have only one place in the Periodic Table and they are generally omitted from the main table and placed by themselves at the bottom of the table starting from Ce(58). It may be assumed

that these elements form a sort of bridge between the preceding and the following elements, i.e. barium and hafnium.

4. Position of the Actinides : This group of elements starting from actimium (89) include all the trans-uranium elements which have been discovered within the last few years. The electronic configurations of these elements have been found to be very similar to that of lanthanides. Both of these groups of elements contain **f** energy levels which are being systematically filled. Thus cerium to lutecium contains $4f^2$ to $4f^{14}$ and the actinide series of the $5f^2$ to $5f^{14}$ is being completed at lawrencium (103). For the same reason, as in lanthanides, the actinides are also placed in the same position of the Periodic Table and are tabulated at the bottom.

5. Oxidation states and the Periodic Table : The position of each element in the Periodic Table emphasizes only one oxidation number for each element. But most of the elements show more than one oxidation numbers.

6. Properties which are not Periodic functions : Certain properties have no relationship with the periodic classification : (i) The activities of the elements expressed in terms of electromotive series (e.m.f. series) do not show periodic variations although this is very useful in explaining many properties of the elements. Elements arranged in the e.m.f. series do not follow any order in the Periodic Table but are scattered throughout the table.

(ii) Some of the elements in the sub-group do not show any likeness in the properties with others. For example, group B copper, silver and gold (IB) have many properties different from those of the alkali metals (IA).

(iii) The specific heat of elements do not give periodic curve but a hyperbolic curve when plotted against atomic numbers.

(iv) Some of the elements in the same group of periodic classification do not belong to the same analytical scheme in qualitative analysis. There are elements widely scattered in the Periodic Table but are included in the same analytical group. For instance, Ba, Sr and Ca of group IIA of the Periodic Table are placed in the same group in the analytical scheme. On the other hand, Pb, Bi, Cu, Cd, Hg, As, Sb, which are widely separated in the Periodic Table, are included in the same group of qualitative analysis. This is mainly due to the

different basis of classification. The analytical scheme is based upon the formation of insoluble compounds under identical conditions by group reagents.

(v) Isotopes and Periodic Table : Isotopes are elements possessing the same atomic numbers but different atomic weights. There are over 1000 isotopes of all the elements occurring in nature or made artificially. Obviously, all these isotopes cannot be accommodated in their respective places. However, the classification based on atomic number has solved this problem.

7. Diagonal Relationships : Lithium, a member of the alkali metal of group IA, in some respects respects resembles magnesium of group IIA. Thus, lithium salts usually occur in hydrated form unlike other alkhali metal salts. Moreover, unlike other alkali metal carbonates and phosphates Li_2CO_3 and Li_3PO_4 are insoluble in water, as are the corresponding magnesium carbonate and phosphate. Lithium is the only alkali metal to form ionic lithium nitride, Li_3N, like magnesium nitride. Thus, Li of group IA resembles Mg of group IIA in many respects contrary to its group properties. Similar relationship exists between the three elements, beryllium of group IIA, aluminium of group IIIA. Boron of group IIIA shows likeness with silicon of group IVA. Thus, the light elements of one group shows similarity in properties with the second elements of the following groups. This similarity is generally referred to as *diagonal relationship* in the Periodic Table as shown below.

I	II	III	IV	V	VI	VII	O	Group
Li	Be	B	C	N	O	F	Ne	
Na	Mg	Al	Si	P	S	Cl	Ar	

The diagonal relationship between the elements may be explained in terms of the electropositive character of the elements. Although an element present in a given group is more electropositive than the corresponding element of the next higher group, the elements become more electropositive in passing down the group. Thus, Li in group IA is more electropositive than Be in group IIA, but Mg is also more electropositive than Be. Thus, both Li and Mg are more electropositive than Be and less electropositive than Na.

The other explanation is based on the sizes of the ions formed by the removal of valence electrons. Thus, Li^+ ion is almost of the same size as Mg^{+2} ion. Similarly, H^+, Be^{+2} and Al^{+3} ions have approximately the same ionic size.

B^{+3} and Si^{+4} also present the same situation. Compounds having similar properties of the elements showing diagonal relationship are formed due to the effect of ionic sizes and their distorting influence on the same anions.

IUPAC approved names of new elements

IPUAC has approved the names for elements 101-109. The final table of names was recommended to IUPAC by the Committee on Nomenclature of Inorganic Chemistry (CNIC) which drew up its original list of names for these elements in 1994.

Atomic number	*Name*	*Symbol*	*Named after*
101	Mendelevium	Md	Dimitri Ivanovich Mendeleev
102	Nobelium	No	Alfred Bernhard Nobel
103	Lawrencium	Lr	Ernest Orlando Lawrence
104	Rutherfordium	Rf	Ernest Rutherford
105	Dubnium	Db	Dubna, site of Russian Laboratory
106	Seaborgium	Sg	Glenn Theodore Seaborg
107	Bohrium	Bh	Neils Bohr
108	Hassium	Hs	Latin for Hesse, the German state
109	Meitnerium	Mt	Lise Meitner

Some of you may be surprised to see that element 105 is here called *dubnium*, because in many textbooks it has been called *hahnium* (Ha) for years. Hahnium was the name proposed by the American researchers, in honour of Otto Hahn. The names for the recently discovered elements 110 to 112 have yet to be decided. (Chemistry Review, Vol 7, No. 4 P. 4, 1994).

QUESTIONS AND PROBLEMS

1. Write an essay on the periodic classification of the elements.
2. Write a note on transition elements.
3. Write a note on periodic law.
4. Discuss the general feature of the Periodic Table and show that these are in conformity with the atomic structure of the elements.

5. Give a brief account of the periodic classification of the elements and discuss how this has systematised the vast informations regarding the chemistry of the elements.
6. Discuss some of the limitations of the Mendeleeffs's periodic classification of the elements.
7. Explain the usefulness of the Periodic Table.
8. Discuss the Periodic Table in terms of the electronic structure of the elements.
9. Discuss the variation of properties of elements in groups and also in periods in the periodic classification of the elements.
10. Write notes on :—(a) Diagonal relationships between elements. (b) The position of rare earth elements in the Periodic Table. (c) Periodic variation of valence electrons. (d) The position of hydrogen in the Periodic Table.
11. Discuss the so-called diagonal relationships in the Periodic Table, with particular reference to the elements Li and Mg, B and Si, O and Cl
12. (a) Discuss briefly the arrangement of extra-nuclear electrons in the different atoms and hence explain the terms "transition" and "inner transition element."

    (b) Describe the properties of rare earths and the position of these elements in the Periodic Table.
13. Write a brief note on diagonal relationship in the Periodic Table.
14. Write detailed notes on group properties of elements.
15. Discuss the following :—
    (a) Alkali metals are highly reactive.
    (b) Elements of zero group are inert.
    (c) Properties of B and Si are similar in many respects.
16. Write explanatory notes on :
    (a) Transition elements.
    (b) Periodic Law.
    (c) Variable oxidation states.
17. Explain the anomalous properties of Li in relation to other alkali metals.
18. Explain why alkali metals react vigorously with water and chlorine.
19. Plot the quantities of the reciprocal values of the first ionization potential for each of the first 18 elements. What is the significance of this graph.
20. Find the relationship between the atomic weights of the following triads of elements :

    Li, Na, K

    F , Cl, Br

    Fe , Ru, Os

CHAPTER 5

THE SHAPES OF MOLECULES

It has been mentioned before that the chemical bonds are directed in space. Thus the electron-pairs forming the chemical bonds are distributed in space around a central metal atom. The electron-pairs, whether they form chemical bonds or not, appear to be responsible for the shapes of the molecules. It has been seen that a molecule has bonding pairs of electrons (shared) and in some cases also non-bonding pairs of electrons. Both the bonding-pairs and lone-pairs of electrons in a molecule around a central atom determine the shape of the molecule. Recently a simple theory has been put forward by Nyholm and Gillespie on the basis of Pauli Exclusion Principles and electron-pair repulsions and has been found to be of great value in accounting for the shapes of a large number of inorganic compounds. With some modifications, this has been found to be quite suitable for the elementary students to understand the basis of molecular structures.

Imagine a system having a positive nucleus round which there are two electrons having the same spin. The positive nucleus will attract the electrons and the two electrons will repel each other. Even the pairing up of the two electrons is not expected since the two electrons have the same spin. Due to the mutual repulsion of the two electrons, they arrange themselves in such a way in the system that the repulsion between these is minimum. The electrostatic repulsion between the two electrons will be minimum when they are separated as far apart as possible. The only way in which these two electrons can have minimum repulsion is to be present on the opposite sides of the nucleus in a straight line passing through the nucleus as shown in Fig. 5—1(a). The situation is the same if two electron-pairs are considered instead of two isolated electrons. The two pairs of electrons will arrange themselves in a similar position in a straight line in order to minimize the repulsion between them. If

the electron pairs are forming two bonds with the central atom, the two bonds will lie in a straight line or at an angle of 180°, because at this position the

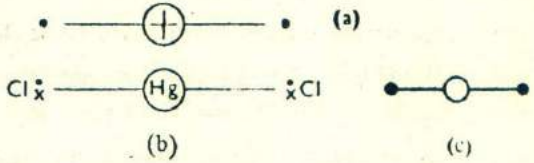


Fig. 5—1 Linear structure : (a) Linear arrangement of two electrons of the same spin around central atom. (b) Linear arrangement of two electron-pair bonds as in $HgCl_2$. (c) Symbolic representation of a linear molecule.

electron-pairs will have minimum of mutual repulsion. Thus the shape of the molecule may be explained on the basis of electrostatic repulsion between-electron pairs.

The pairs of electrons in the valence shell of the central atom in a molecule are always arranged in the same way, i.e., they are as far apart as possible and the molecules assume different shapes which depend only on the number of electron-pairs. The electron pairs may be shared pairs or lone pairs and have great influence in determining the shapes of molecules. It is noted that two electrons-pairs have a linear arrangement, three pairs, a triangular arrangement, four pairs, a tetrahedral, five pairs, in the form of a trigonal bipyramid and six pairs have octahedral arrangement. These arrangements hold good for the non-transition elements, i.e., those which do not use **d** electrons in bond formation. But valence electrons of d^0 and d^{10} behave like non-transition elements as regards the shapes of molecules. It must be remembered that the regular shapes are obtained only when all the electron-pairs are forming bonds with the same kind of atom or group. If some of the electrons are lone pairs or if there are two or more different kinds of atoms or groups attached to the central atom, the regular geometrical shapes become distorted. The geometrical shapes are the consequence of the tendency of the electron-pairs to be apart at a maximum distance so that the interaction between them is minimum. The repulsion between free electron-pairs will be obviously greater than that of repulsion between free electron pairs and a bond pair whereas the repulsion between a bond pair and another bond pair will be least. This theory is known as Valence Shell Electron Pair Repulsion (VSEPR) Theory. The interaction between electron-pairs in the valence shell of the central atom when forming chemical bonds follows the order:

lone pair—lone pair > lone pair—bond pair > bond pair—bond pair
repulsion repulsion repulsion

In short lp—lp > lp—bp > bp — bp (lp = lone pair, bp = bond pair)

Mercury has two electrons in the valence shell ($6s^2$). These electron are used to form two covalent bonds with, say, Cl atoms giving mercuric chloride, $HgCl_2$, as shown in Fig. 5—1 (b). The two bond pairs in $HgCl_2$ arrange themselves as far apart as possible in order to minimize the repulsion between them and the only arrangement is that in which the molecule is linear :

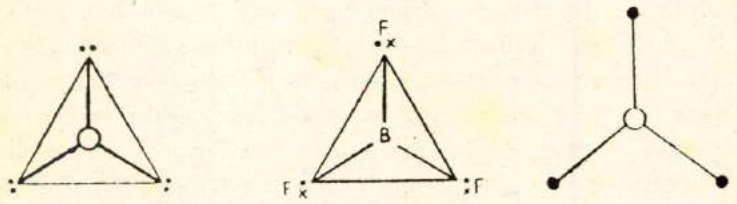
Cl : Hg : Cl Cl—Hg—Cl

Similarly, Be, Zn, Cd, Hg having two electrons in the valence shell form linear molecules of the type A : M : A (i.e. A—M—A). In terms of the molecular orbital they exhibit **sp** hybridization. The case is similar for $[Ag(NH_3)_2]^+$ or $[Ag(CN)_2]^-$ complex ions in which Ag^+ has the completed $4d^{10}$ electron level.

$[NC : Ag : CN]^-$ $[H_3N : Ag : NH_3]^+$

The linear bonds may be represented symbolically as in Fig. 5—1 (c).

The three electron pairs in BF_3 are bond pairs and are situated at the corners of an equilateral triangle for minimum interaction at maximum distance from



(a) (b) (c)

Fig. 5—2. Tringular shape : (a) Tringular arrangement of three electron-pairs : (b) Traingular shape of BF_3 ; (c) Symbolic representation of plane triangular molecule.

one another as shown in Fig 5—2(a) and (b) and symbolically represented in Fig. 5—2 (c).



The angle between F—B—F is 120° which gives the greatest possible separation between the bonded electron-pairs. In terms of molecular orbital B uses sp^2 hybrid orbitals to form the three bonds.

In the case of tin compounds, such as stannous chloride, there is distortion because of the presence of a lone pair. Sn has the valence electrons $5s^2\ 5p^2$. The lone pair occupies one corner of the triangle and the two corners are occupied by



the two bond pairs as given in Fig. 5—3 (a). The lone pair exerts a greater repulsion on the bond pairs resulting in the shortening of the angle Cl—Sn—Cl. Thus the effective shape of $SnCl_2$ molecule in the vapour phase is

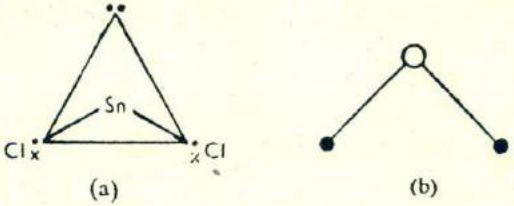
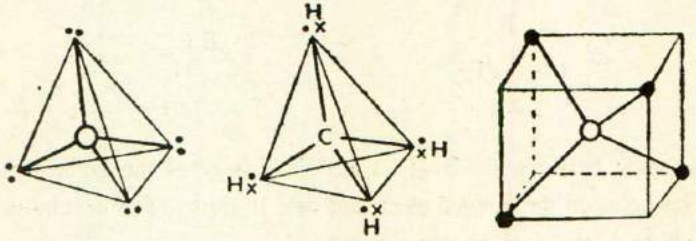


Fig. 5—3 (b). Distortion in triangular molecules : (a) V-shape of $SnCl_2$ due to the presence of a lone pair in plane triangular arrangement. (b) Symbolic representation of a V-shaped molecule.

a V-shape as given in Fig. 5—3 (a) and symbolically represented in Fig. 5—3 (b). The molecular orbital is given by sp^2 hybridization : one of the three m.o. is occupied by the lone pair electrons.

The electrostatic repulsions between four pairs of electrons are at a minimum when these are situated at the corners of a regular tetrahedron as in the case of CH_4 and $SiCl_4$. The angle between H—C—H bond is 109°28′ and is

known as the tetrahedral angle. The Figures 5—4 (a) and (b) represent the tetrahedral shape of the molecule and the geometry of the tetrahedron is given in Fig. 5—4 (c) which gives the perspective view of the distances of the 4 corners

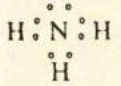


(a) (b) (c)

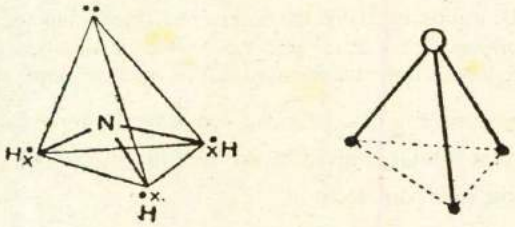
Fig. 5—4. Tetrahedral shape : (a) Tetrahedral arrangement of 4 electron-pairs. (b) Tetrahedral shape of CH_4. (c) Tetrahedral orientation of bonds in space.

from the centre. A very large number of molecules have the tetrahedral shape including complex ions, such as $Zn(NH_3)_4^{+2}$, $Cd(CN)_4^{-2}$ etc. As mentioned before in terms of molecular orbital, the central atom uses sp^3 hybrid orbitals for bond formation. Note that the square planar arrangement of 4 electron-pairs is ruled out because the angles between electron-pairs are 90° which is smaller than the approximate tetrahedral angle 109.5°.

In a molecule of ammonia, there is one lone pair and three bond pairs. The lonepair-bondpair repulsion in ammonia gives it a distorted tetrahedral shape as



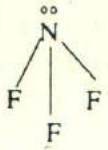
shown in Fig. 5—5(a) and the molecule assumes a trigonal pyramidal arrangement as illustrated in Fig. 5—5 (b). Many other molecules such as PCl_3



(a) (b)

Fig. 5—5. Distortion in tetrahedral molecules due to one lone pair : (a) Trigonal pyramidal shape of NH_3. (b) Symbolic representation of a trigonal pyramidal molecule.

and NF_3 etc. have the same general shape as shown in Fig. 5—5 (b). The bond pairs are under the influence of two positive charge centres of N and H and occupy less volume than the lone pair which is under the influence of only one positive charge centre of N. The lone pair is also close to the central atom, N. Therefore, the lone pair exerts a greater repulsion on the bond pairs in NH_3 distoting the tetrahedral structure and the bond angle H—N—H comes closer to 107.3° instead of the tetrahedral angle 109.5°. If the three H in NH_3 is replaced by F which is more electronegative than H, the charge concentration of the bond pair is shifted towards F atoms in NF_3. The lone pair on N in NF_3 exerts a greater repulsion on the bond pairs and the N—F bonds are further shrunk

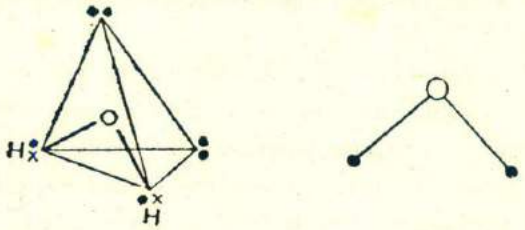


giving F—N—F angle in NF_3 of only 102.1° smaller than H—N—H angle in NH_3. NF_3 like NH_3 has triangular pyramidal shape. In fact, all molecules with three bond pairs and one lone pair have this geometry.

When we look into the electron distributions in water molecúles we find that there are four electron pairs around oxygen and these consist of two lone pairs and two bond pairs.



The four electron pairs are arranged in tetrahedral corners, two corners occupied by the two lone pairs and the other two corners by the two bond-pairs



(a) (b)

Fig. 5—6. Distortion in tetrahedral molecule due to two lone pairs : (V-shape of H_2O ; (b) Symbolic representation of V-shaped molecule.

[Fig. 5—6(a)]. The water molecule has, therefore, a V-shaped structure [Fig. 5—6 (b)]. But the two lone pairs will exert a greater repulsion not only between themselves but also on the two bond pairs and the two O—H in H_2O bonds are forced together closer than N—H bond in NH_3 molecule. The bond angle H—O—H in water molecule is decreased to 104.5°. The situation is the same in F_2O molecule, generally represented by Fig. 5—6(b). Thus an account of the decrease of bond angle in NH_3 and H_2O can be obtained on the consideration that the lone pairs repel the bond pairs increasingly as the number of lone pairs increases.

A central atom having five electron pairs presents a complicated situation. The shape of the molecule with regular arrangement in which there is minimum of repulsion between electron pairs is a trigonal bipyramid as given in

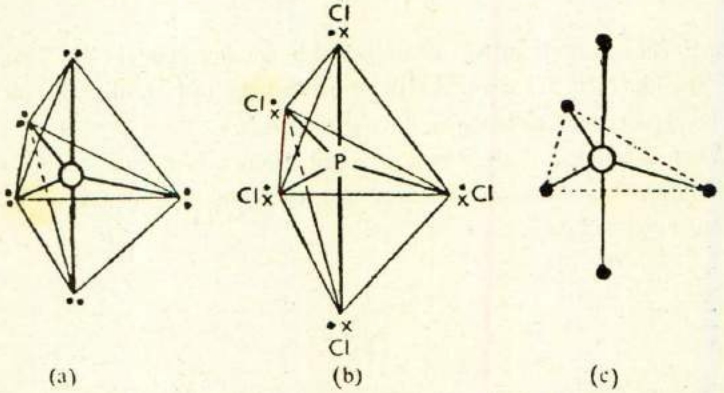
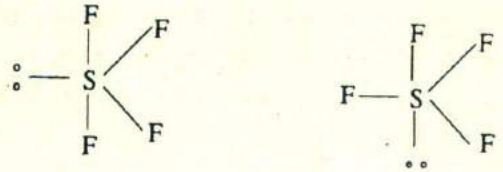


Fig. 5—7. Trigonal bipyramidal shape : (a) Trigonal bipyramidal arrangement of 5 electron pairs. (b) Trigonal bipyramidal shape of PCl_5. (c) symbolic representation.

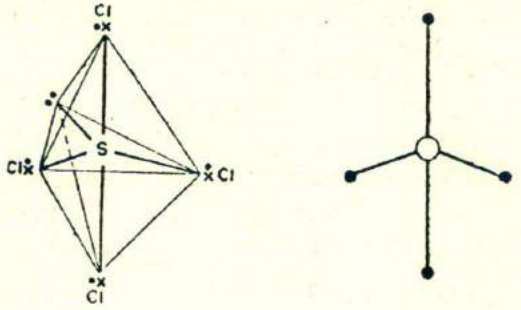
Fig. 5—7 (a). The shape of PCl_5 is a regular triangular bipyramid shown in Fig. 5—7 (b), generally represented by Fig. 5—7 (c) for such molecules like PCl_5, $NbCl_5$, $TaCl_5$ etc. In a trigonal bipyramid, the atoms at the apex (top and bottom) are differently situated as compared to the three equatorial atoms at the corners of a planar triangle. Thus in PCl_5, the angles Cl—P—Cl at the three corners of the planar positions are 120°, whereas the angle Cl—P—Cl involving one Cl at the apex of the bipyramid is 90°. The total number of angles are : 6 angles of 90° each and 3 angles of 120 each.

Now, in the molecules of SF_4, SeF_4 or $TeCl_4$, the valence shell of S, Se and Te contains $3s^23p^4$ and $5s^25p^4$ electron arrangements respectively. The molecules each have total number of 10 electrons involved in bond formation, the same as in PCl_5 but with one lone pair. The bonds in SF_4, TeF_4 or TeF_4 should be directed at the corners of a trigonal bipyramid. But there are two possibilities of the arrangement of the lone pair which may be placed either, (a) at the equatorial position (base) of the pyramid or, (b) at the axial or apical position as shown below :



(a) equatorial (b) axial

In (a) there are four (4) bp—bp angles of 90° and two (2) lp—bp angles of 90°. Also there are one (1) bp—bp angle of 120° and two (2) lp—bp angles of 120°. In (b) There are three (3) bp—bp angles of 90° and three (3) lp—bp angles of 90°. Also there are three (3) bp—bp angles of 120°. Since lp—bp repulsions are greater than bp—bp repulsions it is evident that shape (a) is the preferred arrangement and proved experimentally. Thus the molecules of SF_4, SeF_4 and SCl_4 have four bond pairs and a lone pair as shown in Fig. 5—8(a) for SCl_4. The lone pair occupies an equatorial position because it is at an angle of 90° to two bond pairs only. If the lone pairs is at the apex, this will make an angle

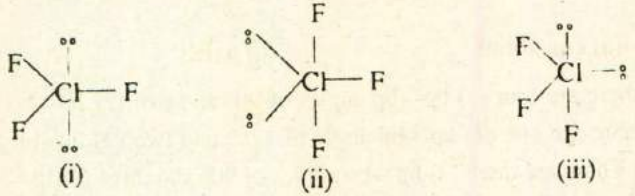


(a) (b)

Fig. 5—8. Distotion in trigonal bipyramidal shape due to one lone pair : (a) Irregular tetrahedral shape of SCl_4. (b) Irregular tetrahedral molecule.

of 90° to three equatorial bond pairs. The lonepair-bondpair repulsion is less when the lone pair is at the equatoprial position and hence the molecules have an irregular tetradedral shape derived from the distortion of trigonal bipyramid as shown in fig. 5—8(b). The six valence electrons each of S, Se and Te might have been distributed in an octahedral positions with bond angles of 90° with the central atom, but there are not enough electron pairs in SF_4, ScF_4 or $TeCl_4$ to form this shape.

Molecules like ClF_3 and BrF_3 in which Cl and Br have s^2p^5 valence electrons have the two lone pairs in the trigonal bipyramid arrangement at the following position ; (i) The two lone pairs at the apical positions at 180°, (ii) the two lone pairs at the equatorial position at 120°, (iii) one lone pair at the apex and the other lone pair at the equatorial position at 90°.



In this case the bondpair-bondpair repulsion is more significant as is seen by the following considerations :—

In (i) the 6 lonepair-bondpair angles are at 90°.

In (ii) there are four lonepair-bondpair angles of 90°and two lonepair-bondpair angles of 120° and lonepair-lonepair angle is 120°.

In (iii) the lonepair-lonepair angle is 90° and, three lonepair-bondpair angles of 90° and two bondpair-bondpair angles of 90°.

Out of the above three possibilities, the most probable shape of the molecule, ClF_3, is that one in which the electrostatic repulsion is minimum and the electron pairs are situated as far apart as possible. From this consideration the two lone pairs must be situated in the equatorial position as shown in Fig. 5—9 (a) or (ii) above, giving the molecule a T-shape, generally represented as in Fig. 5—9 (b). In terms of molecular orbitals the central atom uses sp^3d hybrid bonds.

When the number of lone pairs increases to three in the trigonal bipyramidal structure with five electron pairs as in the case of ICl_2^- ion or tri-iodide I_3^- ion

(as in KI_3), the only possible arrangement for the three lone pairs are the equatorial positions in which these will have minimum of repulsion as given in

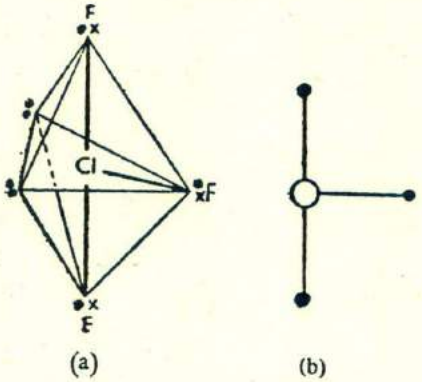


Fig. 5—9. Distortion in trigonal bipyramidal shape due to lone pairs : (a) T-shape of ClF_3 ; (b) Symbolic representation of T-Shaped molecule.

Fig. 5—10 (a). The two iodine atoms are at an angle of 180° and hence the molecule is linear in shape as shown in Fig. 5—10 (b).

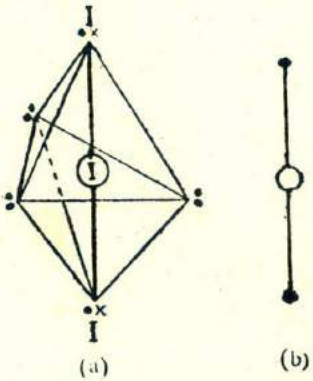
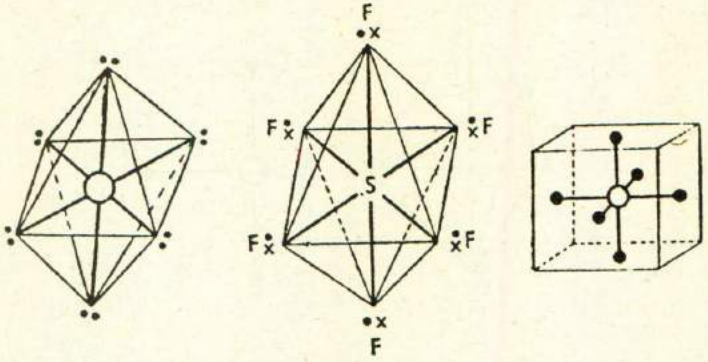


Fig. 5—10. Distortion in trigonal bipyramidal shape due to three lone pairs : (a) Linear shape of I_3^- ion. (b) Symbolic representation.

Molecules, in which the central atom has six electron pair bonds as in SF_6, MoF_6^-, PCl_6^- etc., assume the shape of a regular octahedron as shown in Fig.5—11 (b). It is be evident that the electrostaric repulsion is minimum for

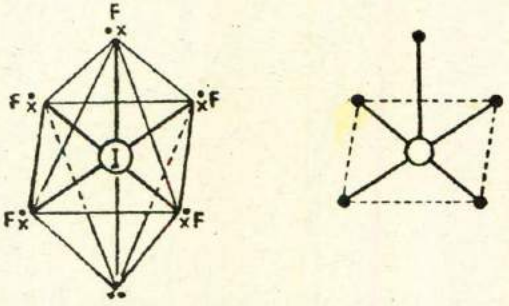
this arrangement of 6 electron pairs and that the bond angles are all 90° as is generally illustrated in Fig. 5—11 (c). In terms of molecular orbital, the central atom uses d^2sp^3 or sp^3d^2 orbitals for bond formation.



(a) (b) (c)

Fig. 5—11. Octahedral shape ; (a) Octahedral arrangement of 6 electron pairs ; (b) Shape of SF_6 molecule ; (c) Octahedral orientation of bonds in space.

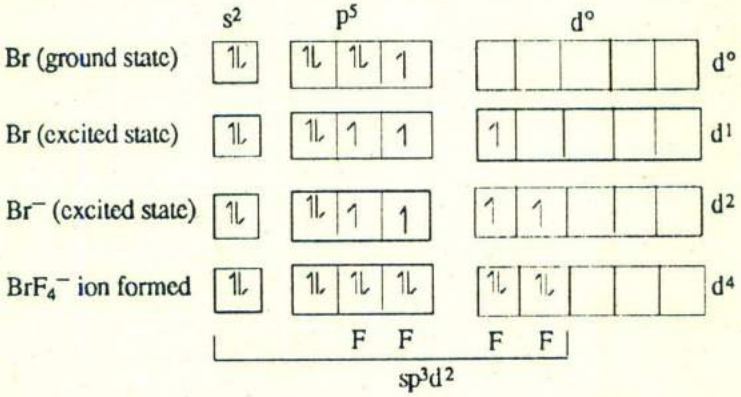
However, if the 6 electron pairs consist of one lone pair and 5 bond pairs, the molecule will assumes the shape of square pyramid as in the case of IF_5, BrF_5, $SbCl_5^{-2}$ shown in Fig. 5—12 (a) and 5—12 (b). If there are 2 lone pairs and 4 bond pairs, obviously the two lone pairs have minimum repulsion if they



(a) (b)

Fig. 5—12. Distortion in octahedral shape due to one lone pair : (a) Square pyramidal shape of IF_5. (b) Symbolic representation of a square pyramidal molecule.

are situated at 180° angle to each other at the two opposite corners. The molecule then assumes a square planar shape as in the case of ICl_4^-, BrF_4^-. Taking BrF_4^- as an example, the valence shell of Br contains s^2p^5 electron arrangement. The formation of BrF_4^- ion can be shown as follows :—



Thus the six pairs of electrons in BrF_4^- or ICl_4^- ions (2 lone pairs and 4 bond pairs) are distributed at the corners of an octahedron. The most probable arrangement for the minimum repulsion between the lone pairs is that in which these are situated at a maximum distance apart at the opposite corners giving square planar structure for ICl_4^- ion as shown in Fig. 5—13(a) and 5—13(b). Thus the square planar shape of a molecule is the result of distortion in the octahedral arrangement. XeF_4 molecule has similar square planar shape [Fig. 5—13 (c)].

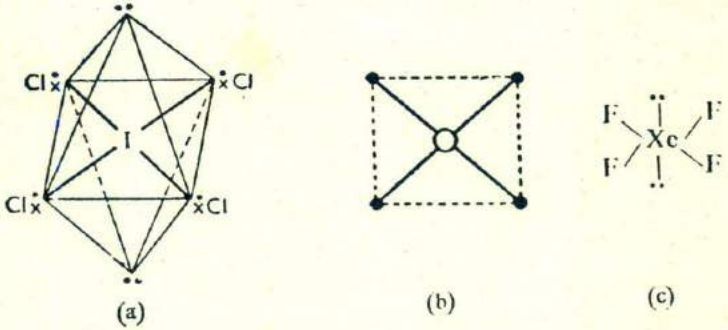


Fig. 5—13. Distortion in octahedral shape due to two lone pairs. : (a) Square planar shape of ICl_4^- ion. (b) Symbolic representation. (c) XeF_4 molecule.

Seven pairs of electrons in a molecule having all the 7 pairs as bond pairs appear to have a pentagonal bipyramidal shape as in the case of IF_7 and ZrF_7^{-3} ion. This is illustrated in Fig. 5—14(a) and 5—14(b). If one of the bond pairs is a lone pair, as in the case of $(SbBr_6)^{-3}$ ion, the shape is distorted to irregular octahedron.

Molecules with more than 6 pairs of electrons have rather complicated shape and are not discussed in this book.

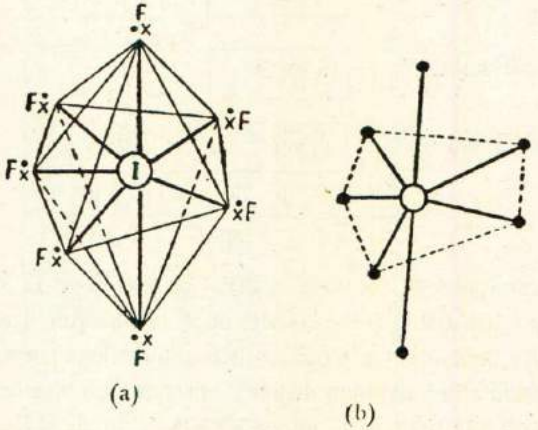


Fig. 5—14. (a) Pentagonal bipyramidal shape of IF_7. (b) Symbolic representation.

The various shapes of molecules on the basis of electron pairs repulsion in the valence shell are summarised in Table 5.1.

Molecules having double and triple bonds have almost similar shapes as those with only single bond. It is to be remembered that double and triple bonds are generally formed by using both σ and π bonds. The shape of a molecule containing an atom with a double or triple bonds is generally determined only by the number of pairs of σ electrons in the valence shell. The effect of π electrons is just ignored. Thus in the molecule of C_2H_4, each C atom has three σ bond pairs and one π bond pair. The most probable arrangement of three σ bond pairs is that in which these are situated with a plane triangular shape. Hence ethylene molecule has a plane triangular shape with the two C atoms at the two centres of the two triangles joined by a double bond.

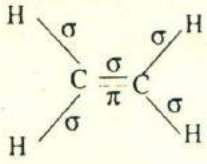
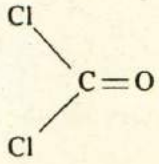


Table 5.1. Shapes of molecules on the basis of electron pairs.

No. of valence shell electron pairs	*Arrangement*	*No. of bond pairs*	*No. of lone pairs*	*Shapes of molecules*	*Examples*
2.	Linear	2	0	Linear	$BeCl_2$, $HgCl_2$, $[Ag(CN)_2]^-$
3	Equilateral	3	0	Triangular plane	BCl_3, BF_3
		2	1	V-shape	$SnCl_2$ (gas)
4	Tetrahedron	4	0	Tetrahedral	CH_4, BF_4^-, $SiCl_4$
		3	1	Trigonal pyramid	NH_3, PCl_3
		2	2	V-shape	H_2O, F_2O
5	Trigonal bipyramid	5	0	Trigonal bipyramidal	PCl_5, $NbCl_5$
		4	1	Irregular tetrahedron	SeF_4, $TeCl_4$, SF_4
		3	2	T-shape	ClF_3, BrF_3
		2	3	Linear	ICl_2^-, I_3^-
6	Octahedron	6	0	Octahedral	SF_6, MoF_6^-
		5	1	Square pyramid	IF_5
		4	2	Square plane	XeF_4, ICl_4^-
7	Pentagonal bipyramid	7	0	Pentagonal bipyramidal	IF_7
		6	1	Irregular octahedral	$[SbBr_6]^{-3}$

Similarly, $COCl_2$ has a planar triangular shape based on the most probable arrangement of three σ electron pairs of C atom.

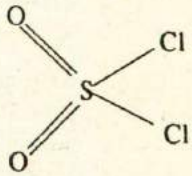


CO_2 has a linear structure because the two σ electron pairs of C are situated at an angle of 180°. In HCN molecule there are two σ bond pairs and two π bond pairs giving a single σ bond between C and H and a single σ bond between C and N and two π bonds between C and N :

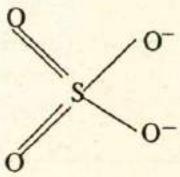
$$H—C \equiv N$$

Since π bond pairs are ineffective, the shape of HCN is linear on the basis of the arrangement of the two σ bond pairs.

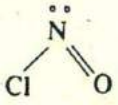
The molecule of SO_2Cl_2 has a tetrahedral shape since the four σ bond pairs of S atom are arranged in this manner :



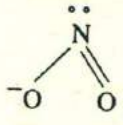
But a double bond consists of two electron pairs, and due to greater repulsion the angle between two adjacent double bonds is greater than that between two single bonds. The angle O=S=O is larger than Cl—S—Cl in SO_2Cl_2. This is applicable in all cases such as SO_4^{-2} ion :

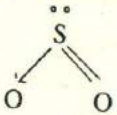


Molecules containing double bonds and also lone pairs are subjected to distortions. But the shapes of such molecules depend mostly on the number of σ bond pairs and are distorted according to the repulsion between the lone pairs and σ bond pairs and also due to lonepair-lonepair repulsion. Thus, NOCl assumes a V-shape or angular structure since the most probable arrangement of three σ electron pairs (two σ bond pairs and one lone pair) is plane triangular but distorted to angular shape because of the presence of a lone pair in the molecule :

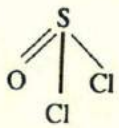


Similar is the case with SO_2 molecule and NO_2^- ion

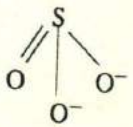




As mentioned before, molecules consisting of four σ electron pairs are tetrahedral in shape. But the presence of lone pair or pairs distort the structure in a similar manner. Thus in the molecule $SOCl_2$ and SO_3^{-2} ion, there are four σ electron pairs (three σ bond pairs and one σ lone pair). The original tetrahedral structures are distorted to triangular pyramidal shape giving :



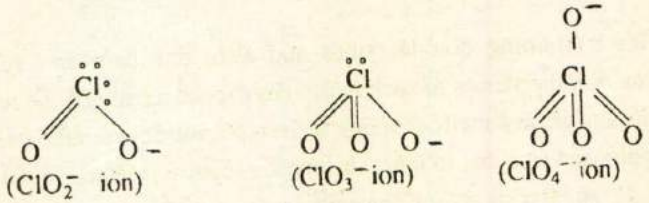
$(SOCl_2)$



$(SO_3^{-2}$ ion)

ClO_2^- ion having two σ bond pairs and two lone pairs (total of four σ electron pairs) is distorted to V-shape :

The molecules with five and six σ electron pairs containing σ lone pairs bring about distortions of trigonal bipyramidal and octahedral shapes respectively. Some of the examples of the shapes of molecules containing double bonds are given in Table 5.2.



(ClO_2^- ion) (ClO_3^- ion) (ClO_4^- ion)

Thus the shapes of molecules containing double and tripe bonds can be predicted by assuming that the two pairs and three pairs of electrons in a double and triple bonds respectively occupy only one of the positions in the various arrangements as predicted in the case of single electron pair bond (single bond) molecules. π electron pairs of double or triple bonds are ignored in determining the shapes of molecules.

Table 5.2 Shapes of molecules containing double and triple bonds.

No. of σ electron pairs	*Theoretical arrangement*	*No. of σ bond pairs*	*No. of lone pairs*	*Shapes of molecules*	*Examples*
2	Linear	2	0	Linear	CO_2, HCN
3	Equilateral triangle	3	0	Plane triangular	$COCl_2$, SO_3 NO_3^-, C_2H_4
		2	1	V-shaped	SO_2, NOCl
4	Tetrahedral	4	0	Tetrahedral	SO_2Cl_2, SO_4^{-2}
		3	1	Triangular pyramidal	$SOCl_2$ SO_3^{-2}
		2	2	V–shaped	ClO_2^-

Thus the important considerations in predicting the shapes of molecules boil down to the following main points :—

(1) The σ bond pairs and lone pairs of electrons in molecules arrange themselves at a maximum distance from one another to minimize the repulsion between them.

(3) The lonepair-lonepair repulsion is much greater than bondpair-bondpair repulsion giving rise to maximum distortion in the shape.

(4). Lone pair also repels bond pairs giving rise to some distortions.

(2) π hond pairs of electrons do not generally determine the shapes of molecules.

(5) A double bond pair repels another double bond pair more than the repulsion between single bond pairs or a double bond pairs-singlebond pair.

(6) Repulsion between bond pair is influenced by the electronegativity of the atoms forming the bonds. The repulsion decreases as the electronegativity values increases.

Shapes of more complicated molecules involving **d** electrons are not discussed in this chapter (see chapter 24 on Complex Compounds).

Comparison of bond hybridization and electron repulsion model of molecules

The bond angles in molecules could be predicted on the basis of hybridization of bond orbitals or the result of electron pair repulsion in valence shell. There appears to be good agreement between the results of the two theories as given in Table 5.3 but departures occur in many cases.

Table 5.3. Bond angles prediction by orbital hybridization and electron pair repulsion.

Number of bonds	*Hybridization*	*Bond angle predicted*	*Number of electron pairs*	*Bond angle predicted*
2	**sp**	180°	2	180°
3	**sp^2**	120°	3	120°
2	**p^2**	90°	4	109°28′
3	**p^3**	90°	4	109°28′
4	**sp^3**	109°28′	4	109°28′
5	**sp^3d, dsp^3**	Trigonal bipyramid	5	Trigonal bipyramid
6	**sp^3d^2 d^2sp^3**	Octahedral	6	Octahedral

Thus in H_2O (105°) NH_3 (107°), the electron pair repulsion gives closer prediction to the tetrahedral angle 109°28′ than the results of bond hybridization model. But the bond angles in H_2S, H_2Se, H_2Te and in PH_3, AsH_3, are closer to those predicted by simple **p** orbital involvement in bond formation. As the

central atom becomes larger in size as in O, S, Se Te or N, P, As and Sb, the electron repulsion appears to decrease to a marked extent and the bond angles in

Table 5.4. Actual bond angles in hydrides and halides.

Predicted : by Hybrid orbitals 90°

by Electron repulsion 109°28′

Molecule	*Bond angle*	*Molecule*	*Bond angle*
H_2O	104.5°	NF_3	102°
H_2S	92.2°	PF_3	104°
H_2Se	91.0°	AsF_3	102°
H_2Te	88.5°	SbF_3	88°
NH_3	107.3°	PCl_3	100°
PH_3	93°	$AsCl_3$	99.5°
AsH_3	91.5°	$BiCl_3$	100°
SbH_3	91.3°	PBr_3	101.5°
		$AsBr_3$	101°
		$SbBr_3$	97°
		$BiBr_3$	100°
		PI_3	98°
		AsI_3	98.5°
		SbI_3	99°

H_2S, H_2Se, H_2Te and in PH_3, AsH_3, SbH_3 molecules approach the value of simple orbital prediction. Some of the values of bond angles are given in Table 5.4 for comparison.

QUESTIONS AND PROBLEMS

1. Show that Al_2Cl_6 molecule is made of two tetrahedra with aluminium atoms at the two centres. Why should it have this structure ?

2. What is the geometry of ozone (O_3) ? How do you explain the shape on the basis of 2 σ bond pairs and 1 lone pair of electrons ?
3. Predict the shape of the following on the basis of electron pair repulsion : N_2O, $SnCl_4$, AsH_3, PH_4^+, CCl_4, XeF_4, XeF_2, PF_5, SeF_6, $PbCl_2$, H_2S and PO_4^{-3}.
4. What shapes do you assign to SO_2 and SO_3 ? The fact that SO_3 has zero dipole moment has been used to conclude about the geometry of the molecule. Explain.
5. What is the effect of lone pair of electrons (non-bonding electrons) on the shapes of molecules ? Illustrate with examples.
6. How the presence of double bonds influences the shapes of the molecules ?
7. The presence of π-bondings has generally been ignored in determining the shapes of a molecule. Why ?
8. Discuss the properties and bonding in water molecule.
9. Give the structure of Al_2Cl_6, PCl_6^-, AlH_4^-, NH_3, SF_4, $PtCl_5$, $SiCl_4$
10. Draw the three-dimensional pictures of the following chemical species showing lone pairs of electrons that occur in a valence level

    SF_6, AsF_5, ClF_3, PCl_4^{-2}

11. Draw the three-dimentional pictures of the following chemical species. Estimate bond angles from the type of symmetry present in each case.

    ClO^- CCl_4, ClO_2^-, ClO_3^-
    ClO_4^- CO_2, N_2, CO
    CN^- C_2^{-2}

CHAPTER 6

TYPES OF CHEMICAL REACTIONS

There are actually quite a large number of different types of chemical reactions that can be distinguished from one another. Attempts have, therefore, been made to classify them into groups. It may be noted that there are again different basis of classification of chemical reactions. Thus chemical reactions may be classified as—

(I) reactions among the atoms and molecules of the same kind;

(II) reactions among the atoms and molecules of different kinds of substances ;

(III) miscellaneous types of reactions.

Chemical reactions may also be classified on the basis of electron transfer phenomenon. Thus we have examples of,

(i) reactions in which there in no electron transfer, and

(ii) reactions in which there is electron transfer from one atom to another.

I. Reactions among the Atoms and Molecules of the Same Kind

1. Isomeric Transformations : In this process the atoms in the molecule of a substance undergo a rearrangement producing a new substance of the same compositions as the original one but with different properties The well-known case of the conversion of ammonium cyanate, NH_4CNO, into urea, $CO(NH_2)_2$, by heat is an example of isomeric change.

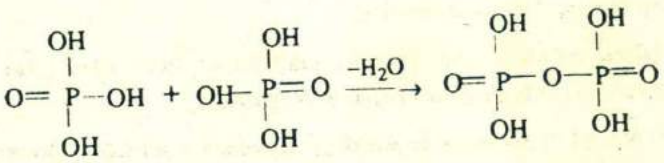
$$NH_4CNO \xrightarrow{\text{heat}} O=C\begin{matrix}NH_2\\ \diagup\\ \diagdown\\ NH_2\end{matrix}$$

The composition of the two substances are the same but arrangements of the atoms in the molecules are different. The cis-and trans-isomers of complexes and organic compounds are other examples.

2. Polymerisation : This process consists of the formation of a large molecule by the combinations of large number of small molecules of the same kind. The product is known as a polymer. Thus ethylene, C_2H_4, is a monomer and polyethylene, $(—HC_2—CH_2—)n$, is a polymer. Sulphur trioxide is a trimer $(SO_3)_3$ and phosphorus pentoxide is a dimer $(P_2O_5)_2$. Sulphur atoms also polymerise to form a chain of sulphur atoms in plastic sulphur. Phosphate, borate and silicate also give polymeric structures.

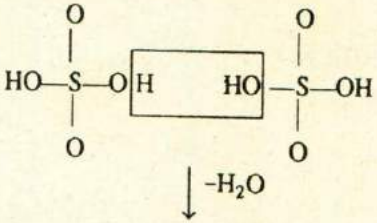
3. Depolymerisation : In this process a polymer or a complex molecule breaks up to give two or more molecules of the same kind. Thus N_2O_4, a dimer, breaks up into two molecules of NO_2.

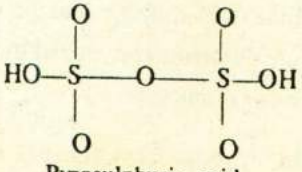
4. Condensation : This process consists of the formation of molecules of a compound with the elimination of water. For instance; two molecules of phosphoric acid combine to form pyrophosphoric acid with elimination of one molecule of water.



2 molecules of orthophosphoric acid — Pyrophosphoric acid

Similarly, 2 molecules of H_2SO_4 undergo condensation :





Pyrosulphuric acid

5. Decomposition : In this reaction the molecule of a substance breaks up into two or more molecules of different substances. Thus when mercuric oxide in strongly heated it breaks up into mercury and oxygen. Similarly, potassium chlorate gives potassium chloride and oxygen on strong heating.

$$2HgO = 2Hg + O_2$$

$$2KClO_3 = 2KCl + 3O_2$$

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

6. Association : In this process two or more molecules of a substance combine together to form a large aggregate. The substance remains unaltered after association and no new substance is formed (compare from polymerisation). for instance, water is an associated liquid whereas H_2S is not and is therefore, a gas at ordinary temperature. The association in water is due to hydrogen bonding. Similarly, acetic acid is an associated liquid in which 2 molecules become associated through hydrogen bonding.

7. Dissociation : This process may be of two types : (a) Thermal dissociation and (b) Ionic dissociation in solution.

(a) Thermal dissociation is a process in which a substance decomposes on heating and the products recombine on cooling. Thus when ammonium chaloride

is heated, it dissociates into ammonia and hydrochloric acid. The latter two recombine again on cooling to produce ammonium chloride.

$$NH_4Cl \underset{\text{cooling}}{\overset{\text{heating}}{\rightleftharpoons}} HCl + NH_3$$

It may be noted that dissociation is a reversible reaction in which the dissociating substance and the products of dissociation are present together in the system in a state of equilibrium. Similarly, the dissociation of PCl_5 follows the equation :

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

(b) Ionic dissociation is a process when a substance breaks up into cations and anions in solutions (say, in water or other solvents). The two ions recombine when the solvent is removed,

$$NaCl \underset{\text{water removed}}{\overset{\text{in water}}{\rightleftharpoons}} Na^+ + Cl^-$$

$$KNO_3 \rightleftharpoons K^+ + NO_3^-$$

The ionic dissociation also gives examples of reversible reactions.

8. Disproportionation : In this reaction a compound undergoes simultaneously oxidation and reduction due to the presence of an element of variable oxidation states. In this process a compound of an element breaks up into two new substances, one containing the element in a lower oxidation and the other containing the same element in a higher state of oxidation. Thus cuprous chloride disproportionates into cupric chloride and elementary copper. Other examples are disproportionation of gold chloride into auric chloride and gold.

Similarly, sodium hypochlorite in solution on heating changes to sodium chlorate and sodium chloride.

From the above examples it is evident that changes in oxidation states of the elements occur during disproportionation reaction. When $\overset{+1}{Cu}$ disproportionates

$$\overset{+1}{Cu_2}Cl_2 = \overset{+2}{Cu}Cl_2 + \overset{0}{Cu}$$

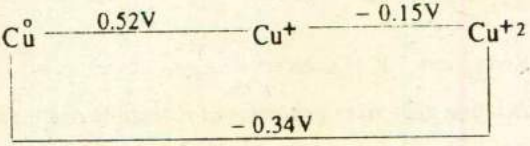
$$3\overset{+1}{Au}Cl = 2\overset{0}{Au} + \overset{+3}{Au}Cl_3$$

$$3\overset{+1}{NaClO} = \overset{+5}{NaClO_3} + \overset{-1}{NaCl}$$

into $\overset{0}{Cu}$ and $\overset{+2}{Cu}$ states, it may be concluded that $\overset{+1}{Cu}$ ions oxidize other $\overset{+1}{Cu}$ ions to form $\overset{+2}{Cu}$ and $\overset{0}{Cu}$. Another definition of disproportionation reaction may be put forward as follows :-

A reaction in which a substance oxidizes itself and also reduces itself is known as disproportionation reaction.

A disproportionation reaction can occur if the standard electrode potential of the couple, say, M^0/M^{+1}, is more negative than that of the couple, M^{+1}/M^{+2}, for a system involving M^0, M^{+1} and M^{+2} ions. Thus the values for coper ions are :-



Thus the force for the conversion of $\overset{+1}{Cu}$ to $\overset{0}{Cu}$ is numerically 0.52 volts. This can happen only if another $\overset{+1}{Cu}$ is converted to $\overset{+2}{Cu}$ for which the value is 0.15V. Since the driving force for conversion of $\overset{+2}{Cu}$ to $\overset{0}{Cu}$ (0.52 volts) is greater than the force required for $\overset{+1}{Cu}$ to $\overset{+2}{Cu}$ (0.15), hence $\overset{+1}{Cu}$ is capable to go spontaneously to $\overset{0}{Cu}$ and Cu^{+2} ion.

II. Reactions Between Atoms and Molecules of different Substances

1. Synthesis : Union of atoms or molecules of two or more different substances to produce a new compound is known as synthesis or synthetic

reaction. Thus when sulphur combines with iron on heating to produce ferrous sulphide, the process involved is synthesis :

$$S + Fe = FeS$$

Similarly, the following examples also show synthetic reactions :

$$2H_2 + O_2 = 2H_2O$$

$$CaO + CO_2 = CaCO_3$$

2. Metathesis or Exchange Reactions : In these reactions two or more substances react which involve displacement of partners to form new substances. These are divided into two groups :

(a) Simple displacement or substitution : In this process one element displaces or substitutes another element from a compound. Thus zinc displaces hydrogen from dilute sulphuric acid to form zinc sulphate and hydrogen is set free :

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

Similarly, iron reacts with copper sulphate solution displacing copper to form ferrous sulphate :

$$Fe + CuSO_4 = Cu + FeSO_4$$

(b) Double decomposition or double displacement : In this process the components of two reacting compounds change places, i. e., doubly displaced. Thus when silver nitrate solution is added to a solution of sodium chloride, sodium nitrate and silver chloride are formed by double displacement :

$$AgNO_3 + NaCl = NaNO_3 + AgCl$$

It may be mentioned that neutralization reactions and hydrolysis may be included in the double displacement type of reactions.

(c) Neutralization : Acids and bases react with one another to form water and ionic compounds known as salts. Thus NaOH reacts with HCl to produce water and NaCl :

$$NaOH + HCl = H_2O + NaCl$$

(d) Hydrolysis : This reaction is more generally defined as the process in which an ion reacts with water to form either H^+ ions or OH^- ions. The effect of water on different substances produces different results. Examples of hydrolytic reactions are :

$$Na_2CO_3 + 2H_2O = 2NaOH + H_2CO_3$$

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

(e) Ammonolysis : This tuype of reaction is analogous to hydrolysis. This is a reaction in which an ion reacts with NH_3 producing compounds containing ammonia residues, i. e., NH_2, NH or N and releasing H^+ ion. Thus when ammonia is added to a solution of mercuric chloride, a white precipitate is obtained which is $Hg(NH_2)Cl$.

III. Miscellaneous Types of Chemical Reactions

There are a large number of chemical reactions which may be classified as miscellaneous types. These, of course, may be included in one or other of the various types described before. Some of them are of great importance in chemistry and are described below.

1. Addition reaction : This is a chemical reaction that involves the addition of the atoms of a molecule to a molecule containing a double bond or a triple bond. These also include reactions in which a molecule is added to another molecule during chemical reaction :

$$CH_2 = CH_2 + H_2 = CH_3—CH_3$$

$FeSO_4, 7H_2O$; $CuSO_4, 5H_2O$ etc. are formed by the addition of water molecules to $FeSO_4$ and $CuSO_4$ respectively and are known as hydrates. This particular type of addition reaction is known as "hydration" reaction. This occurs during crystallization of the products from aqueous solutions.

2. Cracking or Pyrolysis : In this process the thermal decomposition of a large molecule into many different small molecules takes place. Thus C_3H_8 may give by cracking a mixture of C_2H_4 and CH_4 :

$$CH_3—CH_2—CH_3 \longrightarrow C_2H_4 + CH_4$$

Another example is the cracking of petroleum hydrocarbons for the manufacture of gasoline which is a complicated mixture of smaller hydrocarbon molecules.

3. Catalytic reaction : This type of reaction is effected in the presence of a foreign substance which remains practically unchanged at the end. Some reactions which proceed very slowly or do not occur are generally enhanced in presence of the foreign substance. There are also reactions in which the progress of the reaction is arrested or retarded by the foreign substance. Such types of reactions are known as catalytic reactions and the foreign substance is called a catalyst.

Catalysts or catalytic agents can, therefore, accelerate or retard the speed of chemical reactions.

Synthesis of ammonia from nitrogen and hydrogen in presence of tungsten or iron as catalyst is well-known example :

$$N_2 + H_2 \xrightarrow{W \text{ or } Fe} NH_3$$

Similarly, $$SO_2 + O_2 \xrightarrow[V_2O_5]{Pt \text{ or}} SO_3$$

The change of catalyst may produce different types of catalytic reactions giving different products from the same starting reactants. Thus,

$$CO + 2H_2 \xrightarrow{ZnO\ Cr_2O_3} CH_3OH$$

$$CO + 3H_2 \xrightarrow{Ni} CH_4 + H_2O$$

An example of the retardation of a chemical reaction in presence of catalyst is the inhibition of the decomposition of H_2O_2 by addition of a trace amount of acetanilide or borax. Similarly, addition of lead tetraethyl inhibits the explosion rates of gasoline.

4. Chain reaction : In this type of reaction the products of the reaction cause the reaction to continue further. One of the products of reaction is activated by some means and reacts with more molecules and so a chain is formed. Thus

reaction between chlorine and huydrogen molecules takes place in presence of sunlight giving rise to the following chain reaction :

$$Cl_2 \xrightarrow{+ \text{ light } (h\nu)} 2Cl$$

$$Cl + H_2 = HCl + H$$

$$H + Cl_2 = HCl + Cl$$

$$Cl + H_2 = HCl + H, \text{ etc.}$$

5. Photochemical reaction : Certain reactions take place quite readily when the reactants are exposed to light. Such reactions are known as photochemical reactions. A well-known example is the darkening of a photographic film when it is exposed to light and the effect of sunlight on growing plants. The example given in the chain reaction of hydrogen and chlorine forming HCl is also included in the photochemical reaction.

The branch of chemistry that deals with photochemical reactions is known as photochemistry.

6. Induced reaction : Two substances which do not react directly with one another, do, however, react in presence of a third substance which reacts with one of them. Such reactions are known as induced reactions. For example, sodium arsenite and sodium sulphite do not react with each other in aqueous solution. But a solution of sodium sulphite reacts with oxygen of the air when present alone to produce Na_2SO_4. But a mixed solution of Na_2SO_3 and Na_3AsO_3 reacts with each other in presence of air and Na_3AsO_3 is oxidized to Na_3AsO_4 by means of induced reaction :

$$Na_3AsO_3 + Na_2SO_3 \xrightarrow[(air)]{O_2} Na_2SO_4 + Na_3AsO_4$$

Similarly, green $Ni(OH)_2$ is oxidized to black $NiO_2.H_2O$ in presence of Na_2SO_3 :

$$\underset{\text{green}}{Ni(OH)_2} + Na_2SO_3 + O_2 \longrightarrow \underset{\text{black}}{NiO_2.H_2O} + Na_2SO_4$$

7. Exothermic reaction : Reactions accompanied by the evolution of heat are said to be exothermic reactions. The burning of magnesium, carbon, sulphur, methane etc. in air, are all exothermic reactions. Once started, exothermic reaction may proceed in the absence of any supply of energy from outside. Thus, carbon continue to burn in oxygen with the evolution of heat until the supply of carbon or oxygen is exhausted :

$$C + O_2 = CO_2 + 97 \text{ Kcal}$$

$$2Mg + O_2 = 2MgO + 148 \text{ Kcal}$$

$$8Al + 3Fe_3O_4 = 4Al_2O_3 + 9Fe + 800 \text{ Kcal}$$

8. Endothermic reaction : Reactions accompanied by the absorption of heat are known as endothermic reactions. For example, the decomposition of potassium chlorate into potassium chloride and oxygen take place only so long as the compound is heated from outside. Similarly, the reaction of hydrogen and iodine to form hydroiodic acid takes place with absorption of heat. Reactions of this type require a continuous supply of energy from the outside to keep them going :

$$H_2 + I_2 = 2HI - 1.2 \text{ Kcal}$$

$$C + 2S = CS_2 - 1.5 \text{ Kcal}$$

9. Explosion : This is a special type of exothermic combustion reaction which takes place with extreme rapidity. The heat of reaction is liberated almost instantly and usually a large increase in volume results. Thus a mixture of gasoline and air when ignited explodes with great violence. Similarly, the rapid burning of gunpowder results in an explosion.

10. Oxidation and Reduction : In addition to the above reactions there are other types of reactions which may not be included here but are discussed in the appropriate places in this text book. It may be noted that quite a large number of reactions involve electron transfer phenomenon. For this reason the particular type of reactions, known as oxidation and reduction reactions, are dealt in the next chapter separately with some details since these are the most

important reactions in chemistry both from the theoretical and practical points of view.

11. The "electrophilic" and "nucleophilic" reactions : The terms "electrophilic" and "nucleophilic" are often used to describe reactions where covalent bonds are formed.

There are many reactions that result in the formation of new covalent bond and rupture of an old covalent bond. An acid or a base functions as the bond-breaking reagent. Lewis acids are generally known as electrophilic reagents because of the attraction to the electron-rich part of basic molecule. Lewis base behaves as nucleophilic reagent because it attacks the electron-poor region of the acid molecule and supplies electron pair to the nucleus. Base displacements are, therefore, nucleophilic displacement reactions. In the reaction :

$$H_3N: + BF_3 = H_3N: BF_3$$

an electrophilic attack on N by B and also a nucleophilic attack on B by N take place. Similarly, a nucleophilic displacement takes place when H^+ ions react with OH^- ions; $OH^- + H_3O^+ \rightarrow H_2O + H_2O$

Similarly, the displacement of base H_2O from the hydrated complex $[Cu(H_2O)_4]^{+2}$ by a stronger base NH_3 is an example of nucleophilic displacement :

$$[Cu(H_2O)_4]^{+2} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{+2} + 4H_2O$$

An electronphilic displacement occurs when BF_3 reacts with I_2 when I in displaced by B.

$$BF_3 + I_2 \longrightarrow BF_3I + I^+$$

Electrophilic displacement or acid displacement reactions are not so common as the nucleophilic reactions.

Generally, the two types of reaction may be represented as electrophilic displacement :

When H_2O reacts with SO_3, it represents a nucleophilic attack on a double bond :

$$H_2O + \underset{\underset{O}{\|}}{\overset{O}{\|}}{S}=O \longrightarrow H_2SO_4$$

When an aqueous HF reacts with BF_3 an interesting type of reaction known as "push pull reaction" occurs. In this case H_2O pushes HF and BF_3 pulls HF :

$$H_2O + HF + BF_3 \rightarrow [H_3O]^+ + BF_4^-$$

The electrophilic and nucleophilic displacements occur involving electrons in pairs. Sometimes an unpaired electron also gives rise to displacement reactions which is known as "Radical displacement" because upaired electrons give species which are radicals. Thus, when F atoms react with HCl we have Cl° radical. Similarly, OH°- radical is formed during the reaction of Fe^{+2} with H_2O_2:

$$Fe^{+2} + H_2O_2 \longrightarrow Fe(OH)^{+2} + OH^\circ$$

$$F + HCl \longrightarrow HF + Cl^\circ$$

QUESTIONS AND PROBLEMS

1. How will you classify the different types of chemical reactions? Explain some of the important chemical reactions giving examples.
2. Explain :-
   (a) Electrolytic and thermal dissociation.
   (b) Induced reactions.
   (c) Chain reactions.
3. What are the differences between the following types of chemical reactions? Illustrate with examples :—
   (a) Polymerisation and condensation.
   (b) Association and polymerisation.
   (c) Decomposition and polymerisation.
   (d) Ammonolysis and hydrolysis.
   (e) Endothermic and exothermic.

4. Explain the following reactions :—
   (a) Disproportionation reaction.
   (b) Displacement reaction.
5. Write note on different types of chemical reactions.
6. Write short notes on :—
   Association, dissociation and disproportionation.
7. Give a brief account of different types of chemical reactions.
8. Write notes on :—(a) Condensation reactions, (b) Exothermic and endothermic reactions, (c) Induced reactions, (d) Disproportionation reaction.

CHAPTER 7

OXIDATION-REDUCTION REACTIONS

There are many different kinds of chemical reactions, some of which have been discussed in the previous chapter. One very important class of chemical reaction deserves special study and these are oxidation-reduction reactions. Oxidation-reduction reactions are defined according to various concepts.

1. The Classical Concept : According to the classical concept, "oxidation" simply means the addition of oxygen to elements or compounds. This was the original idea about oxidation and likewise the word "reduction" was used to indicate the removal of oxygen from a compound. The definitions were further extended to include other electronegative and electropositive atoms or groups as well as the removal and addition of hydrogen to make the terms more generalized.

(a) Addition of oxygen :

$$2Mg + O_2 = 2MgO$$

$$2CO + O_2 = 2CO_2$$

(b) Addition of electronegative element or group :

$$2FeCl_2 + Cl_2 \xrightarrow{heat} 2FeCl_3$$

$$SnCl_2 + Cl_2 \xrightarrow{heat} SnCl_4$$

$$Cu + S \xrightarrow{heat} CuS$$

Hydrogen peroxide oxidizes an acidified solution of ferrous sulphate to ferric sulphate increasing the proportion of SO_4^{-2} radical :

$$2FeSO_4 + H_2SO_4 + H_2O_2 = Fe_2(SO_4)_3 + 2H_2O$$

(c) Removal of hydrogen :

When H_2S is passed into an acidified solution of potassium dichromate, it is oxidized to sulphur :

$$H_2S \xrightarrow{-H_2} S$$

$$\text{i.e., } H_2S + K_2Cr_2O_7 + HCl \longrightarrow S + CrCl_3 + KCl + H_2O$$

Chlorine is evolved when HCl is heated with MnO_2. Here HCl is oxidized to chlorine :

$$2HCl \xrightarrow{-H_2} Cl_2$$

$$\text{i. e., } 4HCl + MnO_2 \xrightarrow{\text{heat}} MnCl_2 + Cl_2 + 2H_2O$$

(d) Removal of electropositive element or group :

Potassium iodide is oxidized to iodine by the action of hydrogen peroxide. Here K^+ is removed from KI :

$$2KI + H_2O_2 \xrightarrow{-K} 2KOH + I_2$$

Potassium ferrocyanide is oxidized to potassium ferricyanide by removal of K^+ :

$$K_4Fe(CN)_6 \xrightarrow{-K} K_3Fe(CN)_6$$

It can now be easily seen that the definition of the term "reduction" will be just the reverse of that of "oxidation" from the classical point of view.

The term "reduction" may be illustrated by the following reaction.

(a) Addition of hydrogen :

$$2N_2 + 3H_2 = 2NH_3$$

$$S + H_2 = H_2S$$

In the above reactions N and S are reduced to NH_3 and H_2S respectively by addition of H_2.

(b) Addition of electropositive element or group :

Mercuric chloride is reduced to mercurous chloride on heating with mercury. Here the electropositive Hg is added to $HgCl_2$:

$$Hg_2Cle + Hg \rightarrow Hg_2Cl_2$$

(c) Removal of oxygen :

$$CuO \xrightarrow{-O_2} Cu$$

i. e., when hydrogen is passed over heated CuO, it is reduced to Cu by removal of oxygen. Thus,

$$CuO + H_2 = Cu + H_2O$$

Similarly, $Fe_2O_3 + 3C = 2Fe + 3CO$

Fe_2O_3 is reduced to iron by removal of oxygen on heating with carbon.

(d) Removal of electronegative element or group :

$$FeCl_3 \xrightarrow{-Cl} FeCl_2$$

$FeCl_3$ is reduced to $FeCl_2$ by removal of Cl. This can happen in presence of zinc in acid solution or by means of $SnCl_2$. Thus,

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

Similarly, $CuSO_4 + Fe = Cu + FeSO_4$

$CuSO_4$ is reduced to copper by removal of SO_4^{-2} by Fe.

2. Valence state Concept : It will be observed that the oxidation-reduction reactions take place with changes in the valence state of certain atom in the compounds undergoing the reaction. Thus when ferrous chloride is oxidized to ferric choloride, the valence state of iron is increased from divalent to trivalent. Similarly, when H_2S is oxidized to elementary sulphur, the valence state of sulphur is increased from -2 to zero and when CuO is reduced to Cu, the valence state of copper is decreased from +2 to zero. On the basis of valence state, therefore, the following simplified definitions for oxidation and reduction may be put forward:—

Oxidation is a chemical reaction which involves change of valence state in the positive direction.

Reduction is a chemical reaction which involves change of valence state in the negative direction.

3. The Electronegativity Concept : Electronegativity is defined as the tendency for an atom in a molecule to attract electrons. During oxidation-reduction reaction it can be observed that certain atoms in the compounds undergo decrease or increase of electronegativity value. During oxidation there is always a decrease in the electronegativity of an atom, whereas reduction involves increase of electronegativity value. Substances having high electronegativity act as oxidizing agent such as fluorine, halogen, oxygen etc. Substances having low values of electronegativity act as reducing agent, such as hydrogen, sodium, potassium etc.

4. The Charge Concept : Since the terms electropositive and electronegative elements have been used in the classical concept of oxidation-reduction reactions. The following procedure may be adopted to illustrate the phenomena :—

When ferrous salt is oxidized to ferric salt, it can be seen that Fe^{+2} is converted to Fe^{+3}. Similarly, when copper is converted to copper sulphate, $CuSO_4$, the charge on copper increases from zero to +2. When H_2S is oxidized to elementary sulphur, the charge on sulphur is changed from −2 to zero.

(Reduction) $Fe^{+2} \rightleftharpoons Fe^{+3}$ (oxidation)

(Reduction) $Cu^{\circ} \rightleftharpoons Cu^{+2}$ (oxidation)

(Reduction) $S^{-2} \rightleftharpoons S^{\circ}$ (oxidation)

Naturally, when the reaction takes place in the reverse manner i. e.,to the left, this indicates reduction. Hence the following definition :

Oxidation is a process which involves increase of positive charges on an element or removal of negative charges.

Reduction is a process which involves increase of negative charges or decrease of positive charges on an element.

If we examine this definition of oxidation-reduction reaction it is not quite clear as to how this increase of positive charges or removal of negative charges occurs. Obviously, there is no mechanism to consider direct addition of positive

charges to an atom by chemical reaction. Oxidation-reduction reaction is best explained on the basis of electron transfer process as given by the electronic concept.

5. The Electronic Concept : When ferrous chloride is oxidized to ferric chloride by chlorine in aqueous solution, Fe^{+2} is converted to Fe^{+3} and Cl^0 is changed to Cl^-. Similarly, the oxidation of magnesium to MgO involves the change of Mg to Mg^{+2} and of O^0 to O^{-2}. The only way to account for this change is by means of electron transfer process. The electrons in the outermost energy level, i. e., valence electrons in an atom undergo changes during the chemical reaction. The electrons in the outermost energy level may be lost or electrons may be gained depending upon the electronic arrangements of the atom. Thus when Mg^0 is oxidized to Mg^{+2}, the two electrons in the outermost energy level, $2s^2$, are lost. Similarly, oxidation of Fe^0 to Fe^{+2} is due to the loss of two electrons from 4s energy level. Subsequent oxidation of Fe^{+2} to Fe^{+3} is due to the loss of one electron from 3d level which originally contains 6 electrons, i. e., $3d^6$ which has tendency to lose one electron to become $3d^5$ which, now, half-filled represents a stable electronic arrangement.

Now we can give a generalized definition of oxidation :

Oxidation is a process which involves loss of electrons by an atom or an ion.

Similarly, reduction can be attributed due to the gain of electrons by an atom. Thus when oxygen is reduced to O^{-2}, or Fe^{+3} is reduced to Fe^{+2} and subsequently to Fe, the entire process can be easily explained on the basis of gain of electrons by an atom or an ion.

An oxidizing agent is one that accepts electrons and is thereby reduced. A reducing agent is one that gives electrons and is thereby oxidized. Therefore, in oxidation-reduction reactions, electrons are transferred from the reducing agent to the oxidizing agent. The oxidation-reduction reactions (also known as *redox* reactions) are complementary and take place simultaneously. Consequently, oxidation (the loss of electrons) and reduction (the gain of electrons) must always accompany each other in a reaction. In other words, if a given reaction involves an oxidation it must also involve a reduction. Thus the reaction between Mg and oxygen :

$$2Mg^0 + O_2^o = 2Mg^{+2}O^{-2} \text{ or } 2MgO$$

Hence, Mg^0 is oxidized to Mg^{+2} by loss of two electrons and oxygen O^0 is reduced to oxide O^{-2} ion. Mg is the reducing agent and O_2 is acting as an oxidizing agent.

In the reaction between Zn and $CuSO_4$ solution, metallic copper is deposited and some of the zinc rapidly dissolves :

$$Zn^0 + Cu^{+2}SO_4^{-2} = Cu^0 + Zn^{+2}\,SO_4^{-2}$$

Notice that the SO_4^{-2} ion does not undergo any change in this oxidation-reduction reaction. The zinc metal is oxidized from Zn^0 to Zn^{+2} ion obviously by loss of two electrons. The copper ion, Cu^{+2}, is reduced to Cu^0 by the gain of these two electrons. Here Zn^0 is oxidized and acts as the reducing agent and Cu^{+2} is reduced and acts as oxidizing agent.

It may be mentioned here that this is the simplest and at the same time most comprehensive theory of oxidation-reduction reactions that has ever been put forward.

The simple explanation of electron transfer may be readily demonstrated with test tube experiment.

Oxidation-reduction reactions according to the electronic concept is essentially an electrical phenomenon. This means that it should be possible to accomplish oxidation-reduction simply be means of electric energy. The chemical reactions, therefore, can be made to occur by passing electricity through solutions of ions :

$$2Na^+Cl^- \xrightarrow[\text{cruuent}]{\text{electric}} 2Na^o = Cl_2^o$$

Thus, where Na^+ is reduced to Na^o and Cl^- is oxidized to Cl^o and, therefore, represented as,

$$Na^+ + e \xrightarrow{\text{cathode}} Na^o$$

$$2Cl^- - e \xrightarrow{\text{anode}} Cl_2^o$$

Thus electrolysis is a simple electron transfer reaction. These oxidation-reduction reactions do not occur spontaneously but take place only if electrical energy is supplied.

Not only oxiation-reduction can be accomplished by electric current but also, *vice versa*, electricity can be generated by proper arrangements of an oxidation-reduction reaction. Thus the reverse reaction,

$$2Na^{\circ} + Cl_2^{\circ} = 2Na^{+} + Cl^{-}$$

where Na^0 is oxidized to Na^+ and Cl^0 is reduced to Cl^-, takes place spontaneously and spontaneous oxidation-reduction reactions of this sort, which involve the loss and gain of electrons, can actually be used as a means of generating electric current. The arrangements require that electrons lost by Na^0 and gained by Cl_2 pass through a conducting wire during the oxidation-reduction reaction between the two, thereby we can produce a source of electric current. Similarly, the reactions between Zn and H_2SO_4 or $CuSO_4$ solutions produce electric current by the same mechanism of electron transfer from Zn to H^+ ions or Cu^{+2} ion respectively.

Important application of the oxidation-reduction reactions have been made in connection with the manufacture of dry cells, storage batteries and other type of appliances for producing electricity.

Oxidation State and Oxidation Number

When the electrons in the outermost energy level (or valence electrons) are removed from an atom during a chemical reaction, the atom is said to be in a positive oxidation state. Similarly, when an atom takes up electron during a chemical reaction, the atom is said to be in a negative oxidation state. The number of electrical charges on an atom is known as the *Oxidation Number*. Thus in the reaction,

$$Mg^{\circ} + Cl_2^{\circ} = Mg^{+2}\,Cl^{-}Cl^{-},$$

the oxidation number of Mg undergoes a change from zero in the free state to +2 and the oxidation number of chlorine changes from zero in the free state to −1. It may be noted that during oxidation generally the oxidation number of an element is increased and during reduction the oxidation number is decreased. A substance

that causes an increase in the oxidation number of another substance is called an oxidizing agent. A substance that causes a decrease in the oxidation number of another substance is called a reducing agent.

Assignment of Oxidation Number

In connection with oxidation-reduction reaction it is convenient to adopt a generalization in order to assign the correct value for the oxidation number of an element in a compound. Oxidation-reduction reactions are important in chemistry, and writing of balanced equations of these reactions often involves cumbrous process by trial and error method. But the writing of equations has been, for the most part, simplified by adopting the use of oxidation numbers and their changes which occur during oxidation-reduction reactions. The following rules for assigning oxidation number are generally followed :—

(1) Neutral atoms and molecules have zero oxidation number.

(2) When atoms of different elements are present in a molecule, the more electronegative atoms will have a negative oxidation number and the less electronegative atoms have positive oxidation number. Thus,

$$Na^{+1}Cl^{-1},\ H^{+1}Cl^{-1},\ H_2{}^{+1}O^{-2},\ N^{-3}H_3{}^{+1}$$

$$Ca^{+2}S^{-2},\ I^{+1}Cl^{-1},\ Na^{+1}H^{-1}$$

Generally metallic atoms in a compound have positive oxidation number and non-metallic atoms in a compound have negative oxidation number.

(3) Hydrogen is +1 when combined with non-metal and −1 when combined with metals.

(4) Oxygen is −2 except in peroxides when it is −1.

(5) The oxidation number of a compound is always zero. It is determined by the sum of oxidation numbers of the individual atoms, each multiplied by the number of atoms of the element present in the molecule.

In a given compound the sum of the positive oxidation numbers is equal to the sum of the negative oxidation numbers and since the molecule as a whole is neutral, the algebraic sum of the positive and negative oxidation numbers is zero.

Thus knowing the oxidain numbers of some of the well–known elements in a compound, the oxidation number of the unknown can be calculated. For instance, in H_2SO_4, The oxidation number of H is +1 and that of oxygen is –2; the oxidation number of sulphur is easily found out :

$$H_2 \quad S \quad O_4$$

$$2(+1) + x + 4(-2) = 0$$

$$2 + x - 8 = 0$$

$$x = +6 \text{ (oxidation No. of S in } H_2SO_4$$

Similarly, in the case of KNO_3 the oxidation number of N can be calculated as follows :

$$K \quad N \quad O_3$$

$$+1 + x + 3(-2) = 0$$

$$+1 + x - 6 = 0 \quad \text{or } x = +5$$

Some element may exist in several oxidation states and can have several oxidation numbers. Thus nitrogen can have oxidation states :

–3, –2, –1, 0, +1, +2, +3, +4, +5. as in the following compounds :

$$\overset{-3}{NH_3} \quad \overset{-2}{N_2H_4} \quad \overset{-1}{NH_2OH} \quad \overset{0}{N_2} \quad \overset{+1}{N_2O} \quad \overset{+2}{NO} \quad \overset{+3}{N_2O_3} \quad \overset{+4}{NO_2} \quad \overset{+5}{N_2O_5}$$

Similarly, chlorine has oxidation numbers +7, +5,+3, +1, 0 and –1, as in,

$$\overset{+7}{HClO_4} \quad \overset{+5}{HClO_3} \quad \overset{+3}{HClO_2} \quad \overset{+1}{HClO} \quad \overset{0}{Cl_2} \quad \overset{-1}{HCl}$$

Rules for Writing of Equations Involving Oxidation-Reduction Reactions

There are various methods for writing the oxidation-reduction equations and one of the most convenient procedures for balancing such equations is based upon the transfer of electrons. This involves consideration of the change in the oxidation numbers of the elements undergoing oxidation-reduction reactions. The following simple rules provide a convenient means to write the oxidation-reduction equations in the balanced and completed forms.

Rule 1. Indicate the oxidation numbers of each element in the oxidizing and reducing agents in both the states respectively.

Rule 2. Note the elements which undergo a change in the oxidation numbers during the reaction and indicate the electrons gained and lost by them.

Rule 3. Use H^+ ions to form undissociated molecules of water where necessary.

Rule 4. Use H_2O molecules in order to form higher oxygen containing product during oxidation.

Rule 5. Make total number of electrons accepted by the oxidizing agent equal to the total number of electrons given by the reducing agent.

Rule 6. Complete the equation by providing appropriate missing ionic species to form molecules after adding both the sides of the equation and cancelling out equal terms.

Various types of oxidation-reduction reactions have been selected to illustrate the application of the above rules. It may be noted that all the rules may not always be required to write oxidation-reduction equations. Which of the rules will be applicable could be easily determined.

Example 1. Ferrous chloride is oxidized by chlorine to ferric chloride. Writing the change in ferrous chloride and chlorine we get,

$$Cl_2^{\circ} + 2e = 2Cl^-$$

$$Fe^{+2}Cl_2^- - e = Fe^{+3} + 2Cl^-$$

Since the loss and gain of electrons during the process must be equal, the second part has to be multiplied by 2 :

$$Cl_2 + 2e = 2Cl^-$$

$$2Fe^{+2}Cl_2^- - 2e = 2Fe^{+3} + 4Cl^-$$

By adding $2\underline{Fe}Cl_2 + Cl_2 = 2\underline{Fe}^{+3} + 6Cl^-$

or $2FeCl_2 + Cl_2 = 2FeCl_3$

The equation is obtained in the completed and balanced form.

Example 2. H_2S is oxidized to H_2SO_4 when passed into a concentrated aqueous solution of bromine.

Here bromire acts as an oxidixing agent; hence it accepts one electron per atom and is reduced to bromide. When H_2S is oxidized to H_2SO_4 the oxidation number of S is changed from −2 to +6 by loss of 8 electrons.

Now, we find that a higher oxygen containing substance H_2SO_4 is formed by oxidation of H_2S which has no oxygen atom. Hence 4 oxygen atoms in H_2SO_4 will require the use of 4 molecules of H_2O. Thus we write two half-reaction underlining the symbols of those elements which undergo change in the reactions :

$$\overset{0}{Br_2} + 2e = \overset{-1}{2Br}$$

$$\overset{+1}{H_2S^{-2}} - 8e + 4H_2O = \overset{+6}{H_2SO_4} + 8H^+$$

The loss and gain of electrons must be equal. Hence the upper half-reaction is to be multiplied by 4 :

$$4\overset{0}{Br_2} + 8e = 8\overset{-1}{Br} \quad .. \quad .. \quad (1)$$

$$H_2\overset{-2}{S} - 8e + 4H_2O = H_2\overset{+6}{SO_4} + 8H^+ \quad .. \quad .. \quad (2)$$

On adding (1) and (2) we have,

$$4Br_2 + H_2S + 4H_2O = H_2SO_4 + 8H^+ + 8Br^{-1}$$

Completing, $4Br_2 + H_2S + 4H_2O = H_2SO_4 + 8HBr$

Example 3. Potassium dichromate oxidizes potassium iodide in acid solution liberating iodine :

$$\overset{+2+12-14}{K_2Cr_2O_7} + 6e = 2\overset{+3}{Cr} + 2\overset{+1}{K} + 7O^{-2} \quad .. \quad (1)$$

$$2\overset{+1}{K}\overset{-1}{I} - 2e = \overset{0}{I_2} + 2K^{+1} \quad .. \quad .. \quad (2)$$

Now, $7O^{-2}$ require $14H^+$ ions to form $7H_2O$ and, therefore, $14H^+$ is to be introduced in the half -reaction in (1) ; and in order to make the number of

electron lost and gained equal, the half-reaction (2) is to be multiplied by 3. Thus we get,

$$K_2Cr_2O_7 + 6e = 2Cr^{+3} + 2K^{+1} + 7O^{-2}$$

$$7O^{-2} + 14H^+ = 7H_2O$$

$$6KI - 6e = 3I_2 + 6K^{+1}$$

On adding and cancelling equal terms,

$$K_2Cr_2O_7 + 6KI + 14H^+ = 2Cr^{+3} + 8K^{+1} + 7H_2O + 3I_2$$

The above equation is almost complete, except the requirement arising out of the use of H^+ ions. The H^+ ions can come from an acid. Generally the acid used is HCl or H_2SO_4 and hence the anionic portion for the various cations will depend upon the acid used. HCl will gave chlorides and H_2SO_4 will form sulphates. Thus the complete equation is automatically derived :

$K_2Cr_2O_7 + 6KI + 14HCl = 2CrCl_3 + 8KCl + 7H_2O + 3I_2$ or, in the case of H_2SO_4,

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O + 3I_2$$

Example 4. Potassium permanganate oxidizes H_2S in aqueous solution and sulphur is liberated :

$$\overset{+1}{K}\,\overset{+7}{Mn}\,\overset{-8}{O_4} + 5e = Mn^{+2} + K^{+1} + 4O^{-2} \quad (1)$$

$$\overset{+1-2}{H_2S} - 2e = 2H^+ + S^0 \quad (2)$$

Now $4O^{-2}$ require $8H^+$ to form $4H_2O$ and, therefore $8H^+$ is to be introduced in (1) and we get,

$$K\underline{Mn}O_4 + 5e = K^{+1} + \underline{Mn}^{+2} + 4O^{-2}$$

$$4O^{-2} + 8H^+ = 4H_2O$$

$$\overset{+1-2}{H_2S} - 2e = 2H^+ + \underline{S}^0$$

Multiplying (1) by 2 and (2) by 5 in order to make the loss and gain of electrons equal, we have,

$$2K\underline{Mn}O_4 + 10e = 2K^{+1} + \underline{Mn}^{+2} + 8\,O^{-2}$$

$$8\,O^{-2} + 16H^+ = 8H_2O$$

$$5\,H_2\underline{S} - 10e = 10H^+ + 5\,\underline{S}^0$$

On adding, cancelling equal terms and adjusting the species involved we have,

$$2K\underline{Mn}O_4 + 5H_2\underline{S} + 6H^+ = 2K^{+1} + 2\underline{Mn}^{+2} + 5\underline{S} + 8\,H_2O.$$

In order to complete the equation, again it is required to supply the anionic species which will obviously depend upon the acid used. Generally, the acid used is H_2SO_4 because HCl is oxidized by $KMnO_4$ and HNO_3 itself is an oxidizing agent besides an acid.

Hence the complete equation is :

$$2KMnO_4 + 5H_2S + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5S + 8H_2O$$

Example 5. Hot and concentrated nitric acid oxidizes CuS to $CuSO_4$ and NO_2 is evolved :

$$\overset{+1}{H}\,\overset{+5}{N}O_3 + e = \overset{+4}{N}O_2 + H^{+1} + O^{-2} \quad .. \quad (1)$$

$$\overset{+2}{Cu}\underline{S}^{-2} - 8e + 4H_2O = \overset{+2}{Cu}\,\underline{\overset{+6}{S}}O_4 + 8\overset{+1}{H} \quad .. \quad .. \quad (2)$$

One O^{-2} requires $2H^+$ for conversion to H_2O and again (1) has to be multiplied by 8 in order to make the loss and gain of electrons equal. Thus,

$$8HNO_3 + 8e = 8NO_2 + 8H^+ + 8\,O^{-2}$$

$$8\,O^{-2} + 16H^+ = 8H_2O$$

$$CuS - 8e + 4H_2O = CuSO_4 + 8H^+$$

On adding and cancelling equal terms,

$$8H\underline{N}O_3 + Cu\underline{S} = 8\underline{N}O_2 + CuSO_4 + 4H_2O$$

The equation is complete without further adjustment.

Example 6. The oxidation of sodium thiosulphate by iodine :

$Na_2S_2O_3$ is converted to $Na_2S_4O_6$ (sodium tetrathionate) I_2° is converted to iodide $\underline{I}^-$.

Taking +1 as the oxidation number of Na and −2 as the oxidation number of oxygen, the average oxidation number of each S in Na_2SO_3 is +2 and that the average oxidation number of each S atom in $Na_2S_4O_6$ is $2\frac{1}{2}$. Hence,

$$Na_2\overset{+4}{S}_2O_3 \quad = \quad Na_2\overset{+10}{S}_4O_6$$

Thus each S atom of thiosulphate loses $\frac{1}{2}$ electron for oxidation to tetrathionate. 4 S atoms in tetrathionate must come from 2 molecules of thiosulphate. Hence the total change in oxidation number of S is from 2 (+4) = +8 to 4 x $2\frac{1}{2}$ = + 10

$$2Na_2\overset{+8}{S}_2O_3 - 2e = Na_2\overset{+10}{S}_4O_6 + 2Na^+$$

and

$$I_2 + 2e = 2I^-$$

Adding, $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$

Equivalent Weights of Oxidizing and Reducing Substances in Reactions

The fundamental definition of equivalent weight is as follows :—

The equivalent weight of a substance is that weight which combines with or displaces 1.008 parts by weight of hydrogen or 8.000 parts by weight of oxygen. This fundamental definition may be extended and modified to the following definition which seems to be applicable to all ordinary cases.

The gramme-equivalent weight of a substance taking part in chemical reaction is the number of grams of the substance associated with the transfer of N electron or proton or with the neutralization of N negative or positive charge (N is the Avogadro's Number). N may be conveniently replaced by 1 or unity which gives the same result. In acid-base reaction where neutralization reactions occur, protons (H^+) are transferred from the acid to the base and the number of protons transferred determines the equivalent weight of the acid or the base.

The changes in the oxidation numbers of some of the important oxidizing and reducing substances are given in Table 6-1.

Table 6.1. Change in the oxidation numbers of some oxidizing and reducing reagents.

Reagents	*Effective elements*	*Oxidation number of effective element*	*No. of electrons involved*	*Change due to redox reaction*	*New oxidation number of effective element*	*Change in oxidation number*	
$KMnO_4$ (acid)	Mn	+7	+5e	Mn^{+2}	+2	5	
$KMnO_4$ (alk)	Mn	+7	+1e	K_2MnO_4	+6	1	
$KMnO_4$ (neutral)	Mn	+7	+3e	MnO_2	+4	3	
$K_2Cr_2O_7$	Cr	+6	+3e	Cr^{+3}	+3	3	per Cr atom
$KClO_3$	Cl	+5	+6e	Cl^{-1}	−1	6	
$Ce(SO_4)_2$	Ce	+4	+1e	Ce^{+3}	+3	1	
NaClO	Cl	+1	+2e	Cl^{-1}	−1	2	
H_2O_2(redn.)	O	−1	−2e	O_2	0	1	per O atom
H_2O_2(oxn)	O	−1	+2e	O^{-2}	−2	1	per O atom
$FeCl_3$	Fe	+3	+1e	Fe^{+2}	+2	1	
H_2S	S	−2	−2e	S	0	2	
H_2S	S	−2	−8e	H_2SO_4	+6	8	
$SnCl_2$	Sn	+2	−2e	Sn^{+4}	+4	2	
$H_2C_2O_4$	C	+3	−1e	CO_2	+4	1	per C atom
SO_2	S	+4	−2e	SO_4^{-2}	+6	2	
KI	I	−1	−1e	I_2	0	1	per I atom
H_2	H	0	−1e	H^{+1}	+1	1	per H atom
Cu	Cu	0	−2e	Cu^{+2}	+2	2	
Zn	Zn	0	−2e	Zn^{+2}	+2	2	
I_2	I	0	−1e	I^{-1}	−1	1	per I atom

Thus in the reaction,

$$HCl + NaOH = NaCl + H_2O,$$

N protons ($6{\cdot}023 \times 10^{23}$) are transferred from HCl to NaOH. The g. equivalent weights of HCl or NaOH are, therefore, equal to one mole (36·5g.) of HCl and one mole (40·0g) of NaOH. When one mole of H_2SO_4 reacts with 2 moles of NaOH in the reaction:

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O,$$

we have 2N protons transferred from H_2SO_4 to NaOH. hence one gramme-equivalent of H_2SO_4 is equal to g. mole divided by 2, i.e., 98·0/2 = 49·0.

When silver nitrate reacts with sodium chloride, silver chloride is precipitated out according to the reaction,

$$Ag^+NO_3^- + Na^+Cl^- = Ag^+Cl^- + Na^+NO_3^-$$

or,
$$Ag^+ + Cl^- = Ag^+Cl^-$$

The gramme-equivalent weights of $AgNO_3$ and NaCl are calculated from the number of charges neutralized electrically in the reaction. Here 1 positive charge of Ag^+ and 1 negative charge of Cl^- are neutralized. Hence the gramme-equivalent weight of $AgNO_3$ and that of NaCl are equal to one mole of $AgNO_3$ and NaCl (169·89g. and 58·46 g.) respectively. In the case of precipitation of $BaSO_4$ (i.e., $Ba^{+2}+SO_4^{-2} = Ba^{+2}SO_4^{-2}$) one mole of Ba^{+2} ion reacts with one mole of SO_4^{-2}; 2 positive charges and 2 negative charges are neutralized. Hence the gramme-equivalent weight of $BaCl_2$ will be one-half the gramme-formula weight and that of Na_2SO_4 is also one-half the molecular weight.

In the case of oxidation-reduction reactions which always involve transfer of electrons from the substance oxidized to the substance reduced, the equivalent weights are easily calculated. The gramme-equivalent weight of an oxidizing or reducing substance is the weight which loses or gains 1 electron during the process. It may also be put as the weight of the substance which undergoes a change of one unit in the oxidation number of the effective element in the substance. In other words, the gramme-equivalent weight may be obtained by dividing the molecular weight by the total number of electrons transferred or from the total change in oxidation number . Thus,

$$\overset{+7}{KMnO_4} + 5e \longrightarrow Mn^{+2}$$

The change in oxidation number of Mn is 5 or the number of electrons accepted by Mn in $KMnO_4$ is also 5. Hence the gramme-equivalent weight of $KMnO_4$ for this reaction is equal to the molecular weight divided by 5, i.e., 158.02/5 = 31.63g. Similarly,

$$K_2Cr_2O_7 + 6e \longrightarrow 2Cr^{+3}$$

Thus the effective element Cr accepts 6 electrons to change from +6 to +3 state. (The total charge on Cr in $K_2Cr_2O_7$ is 2 x +6 = +12 and $2Cr^{+3}$ has the total charge = 2 x +3 = +6. Hence a change of +12 to +6 involves the gain of 6 electrons.) The change in oxidation number is of 6 units. The gramme-equivalent weight of $K_2Cr_2O_7$ for the reduction to Cr^{+3} state is, therefore, equal to the molecular weight divided by 6. That is, 294.22/6 = 49·037 g.

Similarly, the equivalent-weight of $Na_2C_2O_4$ may be calculated from the reaction

$$\overset{+2}{Na_2}\overset{+6}{C_2}\overset{-8}{O_4} - 2e \longrightarrow 2\overset{+4}{CO_2}$$

The total change in he oxidation number of carbon is from (2 x +3)= +6 to (2 x +4) = +8. This can be accomplished by the loss of 2 electrons. The total change in electron number is also 2. Hence the gramme-equivalent weight of $Na_2C_2O_4$ for this reaction is the molecular weight divided by 2.

The normality of an oxidizing or reducing agent is defined as :

$$\text{Normality} = \frac{\text{No. of electrons gained or lost by 1 g. mole}}{\text{1 litre of solution}}$$

Oxidation-Reduction Potential (Electrode Potential)

Oxidation potential or redox potential is the direct consequence of electron transfer phenomenon of oxidation-reduction reaction. It has been mentioned that electric current can be generated by carrying out oxidation-reduction reactions. When two electrodes are immersed in a solution containing oxidation-reduction system and then connected by a wire, a current flows through the wire from the anode to the cathode. The use of the reactions as a source of electrical energy is possible only if the reactions taking part in the redox reaction are not permitted to come into direct contact. If the reactants come into direct contact, the energy

is liberated as heat energy rather than as electrical energy. The conditions for the generations of electricity are that the cell assembly must have both the electron path between the electrodes via the metallic wire and also the ion path through the solutions. The ion path is generally created via a porous membrane or by suitable connections by a bridge containing ionic solution. The oxidation process always takes place at the anode and reduction at the cathode. It is obvious, therefore, that a chemical reaction involving oxidation-reduction generates electric potential commonly known as redox potential. The values of the redox potentials for the oxidation-reduction system have been determined in most cases and are of great theoretical and practical value. The details of these descriptions may be found in advanced text books on electrochemistry but an elementary qualitative treatment with respect to the applications of oxidation potential to understand the chemical reactions is given here briefly.

Considering the equations :

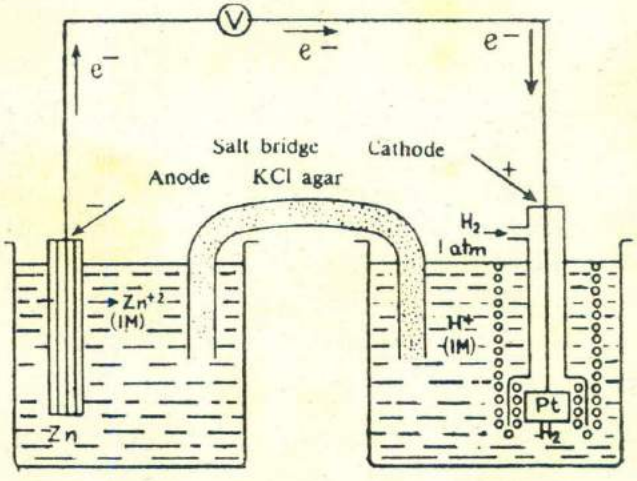
$$Zn + Cu^{+2} = Zn^{+2} + Cu$$

and $$Cu + 2Ag+ = Cu^{+2} + 2Ag$$

we know that the above reactions do take place and we say that Zn is more electropositive than Cu, and Cu is more electropositive than Ag and hence the electropositive metals in solutions are replaced by more electropositive metals. *The term "electropositive" of a metal means the "driving force" with which the metal tends to give up the valence electrons to form a positive ion.* Thus the electropositivity of Zn means the driving force, also known as "Solution Pressure", with which the reaction $Zn = Zn^{+2} + 2e$ takes place. Now, when the driving force is exerted during a reaction, energy must be spent. This means that energy is spent when Zn changes to Zn^{+2} in the reaction $Zn = Zn^{+2} + 2e$. Thus the effective energy content of Zn^{+2} must be less than that of Zn atoms. This effective energy content of a system is known as the "free energy" of the system. The free energy originates from the resultant (or product) of the heat content and tendency for the heat energy to be spent. A system of lower heat content but a higher tendency to spend it will have a higher free energy than one which has a larger heat content but less tendency to spend it. The difference between free energy of Zn and Zn^{+2} is called the change in the free energy that occurs when reaction $Zn = Zn^{+2} + 2e$ takes place. The change in free energy provides the

driving force of the reaction and makes it go. The driving force of a reaction is referred to as "Potential". The reactions involving oxidation, therefore, involves "Oxidation Potential". The oxidation potential, therefore, represents the change in the free energy of reaction. The values of oxidation potential is expressed in volts. More generally the driving force is known as "electrode potential" (E^0). The potential of a standard hydrogen electrode is arbitrarily considered to be zero. The standard hydrogen electrode is made by bubbling H_2 gas at a pressure of 1 atmosphere over platinized platinum immersed in a solution of H^+ ions of 1 M concentration.

To determine the electrode potential of any element, an electro-chemical cell is set up consisting of a strip of the element (say Zn) in contact with a 1 M solution (of Zn^{+2} ions). This is known as the *half-cell* and a standard hydrogen electrode is the other half-cell. The two half-cells connected by a salt bridge (KCl solution in a gel of agar) is shown in Fig. 7—1.



Zinc electrode
$Zn \rightarrow Zn^{+2} + 2e^-$

Hydrogen electrode
$2H^+ + 2e^- \rightarrow H_2$

Fig. 7—1. Electrode Potential

This bridge allows the ions to migrate through it but does not allow the solutions to come in contact. On connecting the two half-cells with a voltmeter,

we can measure the potential difference of the cell as a whole. Each half-cell has the equilibrium reaction :

$$H_2 \rightleftharpoons 2H^+ + 2e$$

$$Zn \rightleftharpoons Zn^{+2} + 2e$$

Because Zn has a greater tendency to go into solution as Zn^{+2}, the zinc acquires a higher electron density than the Pt of hydrogen electrode. Hence the greater electron pressure or electrode potential of Zn causes the electrons to flow to the hydrogen electrode through the wire connection. The flow of electrons from Zn to H increases the electron density at the hydrogen electrode and the equilibrium is shifted to the left causing H^+ ions to be reduced to H_2 :

$$H_2 \leftarrow 2H^+ + 2e$$

At the same time the electron density at the Zn-electrode is decreased, and the equilibrium is shifted to the right and more Zn is oxidized to Zn^{+2} ions :

$$Zn \rightarrow Zn^{+2} + 2e$$

This difference in potential is measured by a voltmeter and is 0.76 volts. The force causing the electrons to move from the Zn-electrode to the H-electrode is called the electromotive force (E.M.F.) and is 0·76 volts. The Zn-electrode is the negative electrode (cathode) because its electron density is higher than that of H-electrode which is the positive electrode (anode). Since the potential of H-electrode is zero, we can say that the potential of Zn-electrode is above 0·76 volt than that of H-electrode. In other words, the sign of Zn-electrode is positive, i.e., + 0·76 volts.

The over-all reaction in the Zn—H cell is one of oxidation and reduction :

Anodic oxidation— $Zn \rightarrow Zn^{+2} + 2e$

Cathodic reduction— $2H^+ + 2e \rightarrow H_2$

Cell reaction— $Zn + 2H^+ \rightarrow Zn^{+2} + H_2$

The cell is represented as :

$$Zn \mid Zn^{+2}\,(1M) \;\overset{e}{\rightarrow}\!\!\!

Table 7.2. E.MF. Series on Oxn-Redn. Potentials.

Elements	*Reduced form*	*Electrode reaction*	*Oxidized form*	*Electrode potential (volts)*
Potassium	K	$\rightleftharpoons$	$K^+ + e$	+ 2·92
Calcium	Ca	$\rightleftharpoons$	$Ca^{+2} + 2e$	+ 2·76
Sodium	Na	$\rightleftharpoons$	$Na^+ + e$	+ 2·71
Magnesium	Mg	$\rightleftharpoons$	$Mg^{+2} + 2e$	+ 2·34
Aluminium	Al	$\rightleftharpoons$	$Al^{+3} + 3e$	+ 1·67
Manganese	Mn	$\rightleftharpoons$	$Mn^{+2} + 2e$	+ 1·05
Zinc	Zn	$\rightleftharpoons$	$Zn^{+2} + 2e$	+ 0.76
Chromium	Cr	$\rightleftharpoons$	$Cr^{+3} + 3e$	+ 0·51
Iron	Fe	$\rightleftharpoons$	$Fe^{+2} + 2e$	+ 0·44
Cadmium	Cd	$\rightleftharpoons$	$Cd^{+2} + 2e$	+ 0.40
Cobalt	Co	$\rightleftharpoons$	$Co^{+2} + 2e$	+ 0·28
Nickel	Ni	$\rightleftharpoons$	$Ni^{+2} + 2e$	+ 0.25
Tin	Sn	$\rightleftharpoons$	$Sn^{+2} + 2e$	+ 0.14
Lead	Pb	$\rightleftharpoons$	$Pb^{+2} + 2e$	+ 0·13
Hydrogen	H_2	$\rightleftharpoons$	$2H^+ + 2e$	− 0·00
Copper	Cu	$\rightleftharpoons$	$Cu^{+2} + 2e$	− 0·34
Iodine	$2I^-$	$\rightleftharpoons$	$I_2 + 2e$	− 0·53
Silver	Ag	$\rightleftharpoons$	$Ag^+ + e$	− 0·80
Mercury	Hg	$\rightleftharpoons$	$Hg^{+2} + 2e$	− 0·85
Bromine	$2Br^-$	$\rightleftharpoons$	$Br_2 + 2e$	− 1·06
Platinum	Pt	$\rightleftharpoons$	$Pt^{+2} + 2e$	− 1·20
Oxygen	$2H_2O$	$\rightleftharpoons$	$O_2 + 4H^+ + 4e$	− 1·23
Chlorine	$2Cl^-$	$\rightleftharpoons$	$Cl_2 + 2e$	− 1·36
Gold	Au	$\rightleftharpoons$	$Au^+ + e$	− 1.68
Fluorine	$2F^-$	$\rightleftharpoons$	$F_2 + 2e$	− 2.85

electrode processes. The equations given indicate that the substance on the left is being oxidized and is acting as a reducing agent. The substances on the right side of the equation are formed and the reactions are proceeding to the right. When the reactions proceed to the left, the substances on the right side are acting as oxidizing agents.

The substances on the top of the table 7.2 are strongest reducing agents and the substances at the bottom are the weakest reducing agents. Thus the lower the oxidation potential, the weaker the reducing ability of the element. The elements at the bottom of table in the right side of the equilibrium equations are the strongest oxidizing agents. Thus the lower the oxidation potential, the stronger the oxidizing ability of the oxidizing agent.

Uses of the E.M.F. Series

The oxidation potential values in the E.M.F. series of elements can be used to determine whether or not a reaction will take place. The most important uses may be mentioned as follows :—

(1) The metal with high electrode potential at the top of the series are good reducing agents. They are the metals most easily oxidized by removal of electrons. They have low electron affinities, low ionization potentials and low electronegativities.

(2) The elements with negative electrode potentials are good oxidizing agents when in the oxidized form, i.e., when the metals are in the form of ions and non-metals are in the form of neutral atoms or molecules.

(3) A reducing agent with a higher potential will reduce any oxidizing agent with a lower potential. The wider the potential difference, the more vigorous will be the reaction. This gives rise to the displacement reaction. To illustrate the application of the rules, the example of the reaction

$$Zn + 2Ag^{+} = Zn^{+2} + 2Ag$$

may be mentioned. The electrodes involved have the following potentials :—

$$Zn = Zn^{+2} + 2e \quad .. \quad .. \quad + 0.76 \text{ volts}$$

$$Ag = Ag^{+} + e \quad .. \quad .. \quad - 0.80 \text{ volts}$$

Therefore, Zn will be oxidized to Zn^{+2} by Ag^+, and Ag^+ will be reduced to Ag by Zn. It means that Ag will be displaced from a solution of, say, $AgNO_3$, by adding Zn metal to the solution (dipping a strip of Zn to the solution of $AgNO_3$). Similarly, H_2 may be prepared by displacement reactions from an acid containing H^+ ions by means of metals which occur above H in the E.M.F. series. Metals with a high positive potential liberate hydrogen from acids with explosive violence and metals with low positive potential liberate hydrogen at a reasonable speed. The displacement reactions are generally applicable and any element will displace other which follows it in the E.M.F. series.

There are two types of cells which make use of oxidation-reduction reactions for generating electricity. They are :—

1. The Primary Cells : These are irreversible cells. The electrodes and electrolytes cannot be restored to their original states once they have been consumed for the production of current by the application of an external electrical potential. The "dry cell" is a primary cell and reactions are irreversible.

2. The Secondary Cells : In these cells the chemicals used and the electrodes may be regenerated after they have been consumed in producing electricity. This is done by passing a direct current of electricity to flow in the reverse direction of the discharge. This is called recharging the cell. The "lead storage battery or accumulators" is an example of secondary cells.

The Dry Cell : The container of the chemicals in this cell is made of Zn which serves as one of the electrodes and is separated from the chemicals by lining with porous paper. A carbon rod in the centre of the cells is the other electrode. The space around the carbon rod contains a mixture of NH_4Cl, MnO_2, $ZnCl_2$ and some saw-dust, all moistened with H_2O in the form of a thick paste. The cells is sealed from top by shellac or pitch. When the dry cell generates electric current, Zn goes into solution as Zn^{+2} ions and electrons accumulate on Zn making it a negative electrode. NH_4^+ ions is reduced at the carbon electrode.

Anode reaction : $Zn \rightarrow Zn^{+2} + 2e$

Cathode reaction : $2NH_4^+ + 2e \rightarrow 2NH_3 + H_2$

Overall reaction : $Zn + 2NH_4^+ \rightarrow Zn^{+2} + 2NH_3 + H_2$

MnO_2 oxidizes H_2, otherwise it will collect and stop the reaction :

$$H_2 + MnO_2 + 2H^+ = Mn^{+2} + 2H_2O$$

The entire reaction :

$$2NH_4^+ + MnO_2 + Zn = 2NH_3 + MnO + H_2O + Zn^{+2}$$

NH_3 formed is taken up by $ZnCl_2$ forming the complex $Zn(NH_3)_4Cl_2$.

The voltage of the dry cell is generally 1·5 volts.

The Lead Accumulator (Storage cell) : The electrodes of lead storage battery consist of two lead plates. The negative plate consists of a spongy lead supported on grid made of Pb-Sb alloy. The positive pole is PbO_2 supported in a similar grid. The electrolyte is H_2SO_4.

When the battery produces current, the following reaction takes place.

At the lead plate :

$$Pb + SO_4^{-2} = \underset{\text{(oxidation)}}{\overset{+2}{Pb}SO_4} + 2e \qquad E^\circ = 0.356 \text{ volts}$$

At the PbO_2 plate :

$$\overset{+4}{Pb}O_2 + SO_4^{-2} + 4H^+ + 2e = \overset{+2}{Pb}SO_4 + 2H_2O$$

(Reduction) $E^\circ = 1.685$ volts

Electrons flow from the lead electrode through the external circuit and enter the lead dioxide electrode. The positively charged lead dioxide is the cathode and the lead electrode is the anode.

Recharging of lead accumulator is done by passing electrons through the cell in the reverse direction by applying an external potential. The lead electrode is now made the cathode. The reaction is :

$PbSO_4 + 2e \rightarrow Pb + SO_4^{-2}$ (reduction)

PbO_2 electrode is made positive and the oxidation reaction is :

$$PbSO_4 + 2H_2O = PbO_2 + 4H^+ + SO_4^{-2} + 2e \text{ (oxidation)}$$

Thus the two processes may be written as :

Pb-plate reaction : $Pb + SO_4^{-2} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} PbSO_4 + 2e$

PbO_2 -plate reaction :

$$PbO_2 + 4H^+ + SO_4^{-2} + 2e \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} PbSO_4 + 2H_2O$$

The overall reaction :

$$Pb + PbO_2 + 4H^+ + SO_4^{-2} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O$$

H_2SO_4 consumed is replenished from time to time.

QUESTIONS AND PROBLEMS

1. Explain oxidation and reduction.
2. Explain what happens when :—
   (a) SO_2 is passed into a solution of Iodine.
   (b) A solution of $Na_2S_2O_3$ is added to acidified $K_2Cr_2O_7$ solution to which KI had been added.
   (c) Iodine reacts with a solution of $Na_2S_2O_3$.
3. Explain the meaning of the term "oxidation state".
4. Define oxidation and reduction in terms of change of oxidation number. What are oxidising and reducing agents ?
5. What are oxidation numbers of nitrogen in each of the following compounds? N_2O, NO, N_2O_3, N_2O_4, HNO_2, NH_3, NH_4Cl, N_2H_4, NH_2OH and AlN.
6. Calculate the equivalent weight of the oxidising and reducing agents in the following reactions in term of the molecular weights of the respective compounds taken as M :—
   (a) $H_2O_2 + KMnO_4 + H^+ \rightarrow Mn^{+2} + H_2O + O_2$,
   (b) $Zn + H^+ + NO^{3-} \rightarrow Zn^{+2} + N_2O + H_2O$,
   (c) $K_2Cr_2O_7 + Fe^{+2} + H^+ \rightarrow 2Cr^{+3} + 2K^+ + Fe^{+3} + H_2O$.
7. What is meant by oxidation-reduction potentials ? How this can be applied for determining the feasibility of chemical reactions ?
8. Write the equations of the following reactions :—
   (a) Chlorine is passed into a solution of ferrous chloride.

(b) H_2S is passed into a neutral solution of $KMnO_4$.

(c) Nitric acid is passed over heated copper.

(d) CuS is heated with strong HNO_3

(e) $KBrO_3$ reacts with KI in acid solution.

(f) $KMnO_4$ reacts with $Na_2C_2O_4$ in acid solution.

(g) H_2O_2 reacts with KI in neutral solution.

(h) $Cr(OH)_3$ reacts with H_2O_2 in presence of NaOH

(i) HCl is dropped over $KMnO_4$,

9. What is meant by the electromotive series of elements? What are the applications if this series ?

10. How do you use electromotive series in the preparation of some elements?

11. Complete and balance the following chemical equations :-

(a) $H_2S + KMnO_4 + H_2SO_4 \rightarrow$

(b) $As_2S_3 + HNO_3 + H_2O \rightarrow$

(c) $SnCl_2 + H_2SO_3 + HCl \rightarrow$

(d) $CrI_3 + KOH + Cl_2 \rightarrow$

12. Write notes on :-

(a) Oxidation and reduction

(b) Oxidation states and oxidation number of elements

13. Give the modern concept of oxidation and reduction , How can you prove experimentally that oxidation and reduction generate electricity ?

14. Discruss with examples (and equation) the disproportionation reactions and oxidation-reduction reactions. Mention their significance in chemistry.

15. Write explanatory note on Electronic Concept of oxidation and reduction.

16. Write note on variable oxidation states.

17. Discuss : Transfer of electrons occur during oxidation-reduction reaction.

18. Discuss the oxidation states of iron and chromium.

CHAPTER 8

OXIDES AND HYDROXIDES

The chemical facts concerning this important class of compounds have now been correlated with electronic arrangements, the ionic sizes, the oxidation states, electronegativity and bonding systems involved in the oxides and hydroxides of the elements.

Compounds containing oxygen as a constituent are most abundant and widely distributed. Among these, oxides of elements (other than halogen and noble metals) are by far the most important from the points of view of chemistry.

OXIDES

Oxides are binary compounds of oxygen and other elements. Oxides of all elements are known:-

The large number of oxides which are formed by various elements are sub-divided into various classes. The classification is based upon two different considerations :-

A. Classification based upon reactions.

B. Classification based upon their structures and bonding systems.

A. Classification of Oxides based on reactions:

(a) Basic oxides, (b) Acidic oxides (c) Amphoteric oxides, (d) Neutral oxides, (e) Sub-oxides (f) Saline oxides (g) Nonstoichiometric oxides (h) Peroxides.

(a) **Basic oxides** : This class includes the normal oxides of most metals. They are derived from the metallic elements and their properties depend upon the degree of electropositive character of the metal. Basic oxides form salt and water

with acids, Basic oxides when soluble in water produce aqueous solutions of bases. For instance , Na_2O, CaO, MgO., Fe_2O_3 etc. are basic oxides. The ionic oxide are generally basic. The smaller the positive charge and larger the size of the element forming the oxide, the greater is the basic character, Thus K^+ forms a strong basic oxides than Mg^{+2} ion, Oxides of elements having low electronegativity values are more basic than those having high electronegativity values. Thus CaO is more basic than Al_2O_3

Method of Formation of Basic Oxides

(i) The alkali metals take up oxygen from the air and are converted into oxides. The alkali metal oxides, however, are generally prepared by heating excess of the alkali metal with oxygen in vacuo having :

$$\underset{\text{(Excess)}}{Na + O_2} \xrightarrow[\text{vacuo}]{\text{heated in}} \underset{\text{Excess Na removed}}{Na_2O + Na}$$

(ii) The alkaline earth metal oxides are generally prepared by strongly heating their hydroxides, carbonates and nitrates, e.g.

$$CaCO_3 \xrightarrow[812^\circ]{\text{heat}} CaO + CO_2$$

(iii) Heavy metal oxides are generally prepared by heating the metal or lower oxides in air. They are also formed by heating the hydroxides, carbonates, nitrates etc. For instance,

$$Cu + O_2 \xrightarrow{\text{heat}} CuO$$

$$Cu_2O + O_2 \xrightarrow{\text{heat}} CuO$$

$$Cu(OH)_2 \xrightarrow{\text{heat}} CuO + H_2O$$

$$2Cu(NO_3)_2 \xrightarrow{\text{heat}} 2CuO + 4NO_2 + O_2$$

$$CuC_2O_4 \xrightarrow{\text{heat}} CuO + CO_2 + CO$$

Reactions :

(i) Basic oxides react with acids to form salts and water :

$$Na_2O + 2HCl = 2NaCl + H_2O$$

$$CaO + 2HCl = CaCl_2 + H_2O$$

$$FeO + H_2SO_4 = FeSO_4 + H_2O$$

(ii) Some of the basic oxides produce hydroxides with water and when soluble they are extensively dissociated to give strong alkaline reactions :

$$Na_2O + H_2O \longrightarrow 2\,NaOH \xrightarrow{aq.} Na^+ + OH^-$$

$$CaO + H_2O \longrightarrow Ca(OH)_2 \xrightarrow{aq.} Ca^{+2} + 2OH^-$$

(iii) Oxides of the teavy metals are decomposed to metal when heated with carbon or hydrogen :

$$Fe_2O_3 + 2C = 2\,Fe + CO_2 + CO$$

$$Fe_2O_3 + 3H_2 = 2\,Fe + 3\,H_2O$$

But the alkali and alkaline earth metal oxides do not undergo above reactions.

(iv) Some of the oxides of less electropositive elements are easily decomposed by heat into metal and oxygen :

$$2\,Ag_2O \xrightarrow[\text{or light}]{\text{heat}} 4\,Ag + O_2$$

$$2\,HgO \xrightarrow{\text{heat}} 2\,Hg + O_2$$

(b) **Acidic oxides** : The acidic oxides are generally derived from non-metals. They react with bases to form salt and water, and sometimes only salt. They are anhydrides of the respective acids and their hydroxides are oxyacids. For instance, SO_2, SO_3, N_2O_5, P_2O_5, B_2O_3 etc. are some of the acidic oxides. Elements with high electronegativity values form acidic oxides.

Acidic oxides are also formed by metals which can exert a high oxidation state by losing a number of electrons and thus combine with several oxygen atoms. Thus CrO_3, SnO_2, WO_3, MoO_3, etc. are examples of metallic acidic oxides. Elements having both metallic and nonmetallic properties, i e., metalloidic elements, also produce oxides which are acidic, such as, As_2O_3, Sb_2O_3, SiO_2, etc.

Both the non-metallic and metallic acidic oxides when soluble in water are extensively hydrolysed and produce acidic reactions.

Reactions :

(i) The acidic oxides react with water to give the respective acids :

$$SO_2 + H_2O = H_2SO_3$$

$$SO_3 + H_2O = H_2SO_4$$

$$N_2O_5 + H_2O = 2HNO_3$$

$$P_2O_5 + 3H_2O = 2H_3PO_4$$

$$CO_2 + H_2O = H_2CO_3$$

$$B_2O_3 + 3H_2O = 2H_3BO_3$$

$$CrO_3 + H_2O = H_2CrO_4$$

$$WO_3 + H_2O = H_2WO_4$$

$$MoO_3 + H_2O = H_2MoO_4$$

$$As_2O_3 + 3H_2O \longrightarrow 2H_3AsO_3$$

$$\longrightarrow H_3AsO_4$$

$$Sb_2O_3 + H_2O \longrightarrow H_3SbO_3$$

$$\longrightarrow H_3SbO_4$$

(ii) Acidic oxides combine with bases to form salts and water. Thus,

$$CO_2 + Ba(OH)_2 \longrightarrow BaCO_3 + H_2O$$

$$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$$

$$N_2O_5 + NaOH \longrightarrow NaNO_3 + H_2O$$

(c) Amphoteric oxides : The amphoteric oxides react with both acids and alkalies and, therefore, exhibit both acidic and basic properties. Thus, Al_2O_3, ZnO, SnO, Cr_2O_3 etc. are examples of amphoteric oxides. These oxides are generally insoluble in water and dissolve readily in an acid or a base.

Reactions :

(i) With acids these form salt and water. Thus,

$$Al_2O_3 + 6\,HCl = 2\,AlCl_3 + 3\,H_2O$$

$$ZnO + 2\,HCl = ZnCl_2 + H_2O$$

$$SnO + 2\,HCl = SnCl_2 + H_2O$$

$$Cr_2O_3 + 6\,HCl = 2\,CrCl_3 + 3\,H_2O$$

(ii) The same oxides react with alkalis to give salt and water. Thus,

$$Al_2O_3 + 2\,NaOH = 2\,NaAlO_2 + H_2O$$
$$ZnO + 2\,NaOH = Na_2ZnO_2 + H_2O$$
$$SnO + 2\,NaOH = Na_2SnO_2 + H_2O$$
$$Cr_2O_3 + 2\,NaOH = 2\,NaCrO_2 + H_2O$$

(d) Neutral oxides : The neutral oxides combine neither with acids nor with bases to form salts. They do not give acidic or basic reactions. Thus, H_2O, CO, N_2O, NO etc. are examples of neutral oxides.

(e) Sub-oxides : The sub-oxides or protoxides generally contain less number of oxygen atoms than what is actually required for the formation of normal oxides. Thus, Pb_2O, Ag_4O, Cu_4O, Pd_2O etc. are examples of sub-oxides.

(f) Saline oxides : The saline oxides are so called because they behave like salts. These are also known as *compound oxides* and *mixed oxides* since these may be assumed to be a combination of more than one oxide. Thus, Au_2O_2, Fe_3O_4, Pb_3O_4, Mn_3O_4, NO_2 etc. are examples of saline oxides. They are generally formed by combination of a basic oxide with an acidic oxide. Ferroso-ferric oxide, Fe_3O_4, may be considered as a combination of FeO and Fe_2O_3, and with acids it gives salts of both ferrous and ferric ions. Mixed-metal oxides are known as spinels having special types of crystal structures.

Similarly, red lead, Pb_3O_4, is composed of PbO and PbO_2 and Mn_3O_4, is composed of MnO and MnO_2. NO_2 is a mixed anhydride of N_2O_3 and N_2O_5. These combinations may be represented as follows :

$$Au_2O_2 = 2AuO$$
$$Fe_3O_4 = FeO.Fe_2O_3 \text{ or } Fe\,Fe_2O_4$$
$$Pb_3O_4 = 2PbO.PbO_2 \quad \text{or} \quad PbPb_2O_4$$
$$Mn_3O_4 = 2MnO.MnO_2 \text{ or } MnO.Mn_2O_3 \text{ or } MnMn_2O_4$$
$$4NO_2 = N_2O_3.N_2O_5$$

(g) Nonstoichiometric oxides : There are also many oxides which are known as nonstoichiometric oxides. These are generally formed by metals having variable oxidation states. Thus ferrous oxide probably never has the

composition FeO, but usually something in the range $FeO_{0.9}$ to $FeO_{0.95}$ depending on the manner of preparation.

(h) Peroxides : These are oxides which contain more oxygen combined to an element than what is necessary for its highest oxides according to the periodic law. In terms of the oxidation states of oxygen, peroxides contain oxygen in $-\frac{1}{2}$ and -1 oxidation states. The most common oxidation sate of oxygen in normal oxides is–2. Exceptions are O_2F_2 and OF_2.

Classification of Peroxides Based on Reactions

Peroxides have been classified into the following groups on the basis of their reactions :—

(I) Basic Peroxides.

(II) Acidic Peroxides.

(III) Neutral Peroxides.

(I) Basic Peroxides : The basic peroxides when soluble in water produce hases. Na_2O_2, KO_2, CaO_2, BaO_2 are examples of water-soluble basic peroxides.

PbO_2, Bi_2O_5, MnO_2 etc. are, however, not true basic peroxides, because the oxygen content does not exceed that of the normal typical oxides. But these are classified as basic peroxides, because these react with acids to produce salts of the basic oxides of PbO, Bi_2O_3 and MnO respectively.

Reactions :

(i) Basic peroxides react with water to form hydrogen peroxides or oxygen in addition to bases :

$$Na_2O_2 + 2\,H_2O = 2\,NaOH + H_2O_2$$

$$2\,Na_2O_2 + 2\,H_2O = 4\,NaOH + O_2$$

(ii) With sulphuric acid these peroxides always give oxygen :

$$2\,MnO_2 + 2\,H_2SO_4 = 2\,MnSO_4 + 2\,H_2O + O_2$$

(iii) With hydrochloric acid, chlorine is always evolved :

$$BaO_2 + 4\,HCl = BaCl_2 + 2\,H_2O + Cl_2$$

$$MnO_2 + 4\,HCl = MnCl_2 + 2\,H_2O + Cl_2$$

Chlorine evolved is equivalent to the excess amount of oxygen present in the basic oxides. This amount of oxygen is generally known as the "available oxygen" of the peroxides.

(iv) The basic peroxides form salts by direct union with acidic oxides :

$$Na_2O_2 + SO_2 = Na_2SO_4$$

$$PbO_2 + SO_2 = PbSO_4$$

(II) Acidic Peroxides : The acidic peroxides generally produce typical acids in presence of water by loss of oxygen. CrO_4, S_2O_7, Cl_2O_7, SnO_3, Cl_2O_2, ClO_2, UO_4 etc. are examples of acidic peroxides.

Reactions :

(i) With water the acidic peroxides react to form normal acids with the evolution of oxygen :

$$2\,S_2O_7 + 4\,H_2O = 4H_2SO_4 + O_2$$

$$2\,CrO_4 + 2H_2O = 2H_2CrO_4 + O_2$$

(ii) With sulphuric acid oxygen is evolved :

$$2\,CrO_4 + 3H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3\,H_2O + O_2$$

(iii) Acidic peroxides form salts with alkali oxides with the evolution of oxygen :

$$CrO_4 + Na_2O \longrightarrow Na_2CrO_4 + O_2$$

$$S_2O_7 + Na_2O \longrightarrow Na_2SO_4 + O_2$$

(III) Neutral Peroxides : As the name implies, it is neutral and has neither basic nor acidic characteristics. A well-known example is H_2O_2.

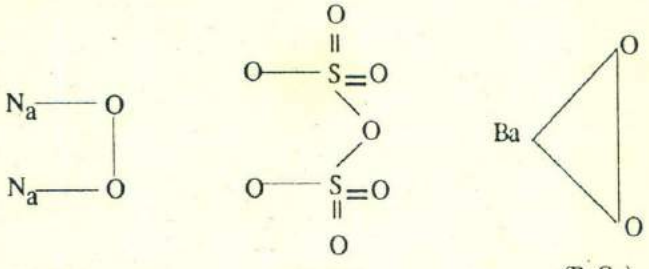
Classification of Peroxides Based Upon Structures

The classification of peroxides on a structural ground depends upon the oxidation state of the elements combining with oxygen. It has been assumed that the oxygen atom or atoms over and above those required to form the normal oxide may either be doubly linked to the metal atom or singly linked to both the metal and oxygen atom.

(i) The peroxides having the excess oxygen atom or atoms doubly linked to metal atom are known as "*polyoxides*".

$$O = Pb = O \qquad O = Mn = O$$

(ii) The peroxides having the excess oxygen atom or atoms singly linked to the metal and oxygen, forming a chain or ring are "*normal peroxides*". These contain oxygen in −1 oxidation state.



(Na_2O_2) (S_2O_7) (BaO_2)

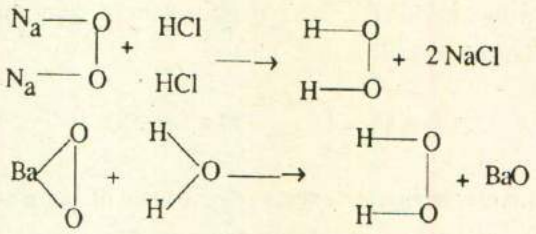
The direct oxygen-oxygen bonds in normal peroxides usually break down at high temperatures. Mostly electropositive metals form peroxides having O_2^{-2} ion which contains no unpaired electrons.

(iii) Oxides of alkali metals, such as K, Rb and Cs, contain oxygen with oxidation number $-\frac{1}{2}$ and are called *superoxides*. These have the general formula MO_2 (KO_2, RbO_2 CsO_2). These are ionic solids having M^+ cation and O_2^-, anion. These are coloured solids having magnetic properties and contain unpaired electrons. It is to be noted that superoxide ion, O_2^-, exists only in the solid state but gives O_2 and H_2O_2 in water :

$$2KO_2 + 2H_2O = O_2 + H_2O_2 + 2KOH$$

Polyoxides, peroxides and superoxides can be distinguished from one another by the actions of water or dilute acids upon them.

(i) Peroxides have group —O—O— and hence yield H_2O_2 as a characteristic product with water or dilute acid :



Superoxides produce H_2O_2 and also O_2 gas with water :

$$2\,RbO_2 + 2H_2O = O_2 + H_2O + 2RbOH$$

(iii) Polyoxides are not attacked by dilute acids and not at all by water. but with strong HCl or H_2SO_4 produce chlorine and oxygen respectively :

$$2\,O{=}Mn{=}O + 2H_2SO_4 \longrightarrow 2\,MnSO_4 + 2H_2O + O_2$$

$$2\,O{=}Mn{=}O + 8HCl \longrightarrow 2\,MnCl_2 + 2\,Cl_2 + 4H_2O$$

(iv) Both peroxides and superoxides also produce chlorine or oxygen when acted upon by strong HCl or H_2SO_4 but by a different mechanism :

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$

$$2H_2O_2 = 2H_2O + O_2$$

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2$$

$$H_2O_2 = H_2O + O$$

$$2\,HCl + O = H_2O + Cl_2$$

The distinguishing reactions of polyoxides, peroxides and superoxides are given in Table 8·1.

Table 8·1. Distinction between Peroxides, Polyoxides and Superoxides.

Reagents	*Peroxides* O_2^{-2}	*Superoxides* O_2^{-1}	*Polyoxides* O_2^{-2}	*Normal oxide* O^{-2}
1. Water	H_2O_2	$H_2O_2 + O_2$	No reaction	OH^-
2. Dil. Acids	H_2O_2	$H_2O_2 + O_2$	No reaction	
3. Conc. HCl	Cl_2	$Cl_2 + O_2$	Cl_2	
4. Conc. H_2SO_4	O_2	O_2	O_2	

B. Classification of Oxides on the Basis of Bonding Systems

There are three classes of oxides on the basis of the nature of chemical bonds.

(i) Ionic Oxides	(ii) Covalent Oxides	(iii) Intermediate Oxides
e.g. Li_2O	*e.g.* SO_2	*e.g.* Fe_2O_3
BaO	CO_2	ZnO
MgO	CO	BeO
CaO	Cl_2O_7	

The ionic oxides are generally formed by the alkali and alkaline earth metals.

The covalent oxides are mostly formed by the the non-metals.

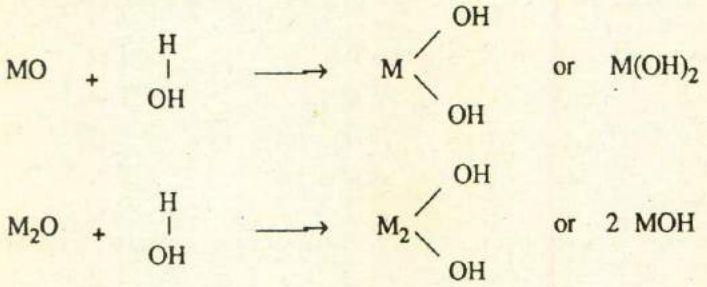
The transition metals and many other heavy metals form oxides containing bonds which are conveniently regarded as being intermediate between ionic and covalent bonds.

The ionic oxides when soluble in water give bases due to dissociation into ions. Whereas the covalent oxides of the non-metals are usually acidic, dissolving in water to produce solutions of acids. These oxides are, therefore, known as acid anhydrides. The ionic oxides function as basic anhydrides. Many of the intermediate oxides do not react appreciably with water and some of them show characteristic of both acids and bases generally known as amphoteric.

Elements having large positive oxidation number tend to form covalent oxides. Thus, CO_2, SO_3, Sb_2O_5, Cl_2O_7 are some of the covalent oxides. If an element forms more than one oxides the covalent oxide will be that having the element in the highest oxidation state. Thus, As_2O_5 having +5 arsenic is more covalent (more acidic) than As_2O_3 containing +3 arsenic. SO_3 having S in +6 state is more acidic than SO_2 having S in +4 state. Similarly, CrO_3 is acidic, Cr_2O_3 amphoteric and CrO distinctly basic. Covalency is also favoured by the small size of the positive ion. Hence, BeO is almost covalent oxide as compared to the strongly basic BaO containing large barium ion.

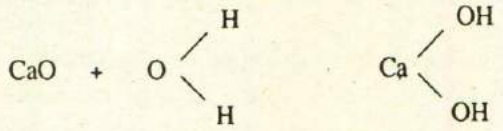
HYDROXIDES

Hydroxides are compounds of oxides with water. Thus, the following examples illustrate the formation of hydroxides of an element by the combination of its oxides with water :



The stability and definiteness of the hydroxides depend upon the reversibility of the above reactions. Definite and stable hydroxides are formed by those elements which are most electropositive and most electronegative. These can be isolated in the free state and have great stability when heated.

The hydroxides or hydroxy compounds are important class of compounds containing hydrogen, oxygen and at least one other element. They can often be made by the reaction of water with an oxide. Thus, when calcium oxide, CaO, is treated with a limited amount of water, the product is solid calcium hydroxide, $Ca(OH)_2$:



Solutions of sodium hydroxide, NaOH, and calcium hydroxide are alkaline, but not all hydroxy compounds are alkaline and also not all of them are soluble in water. Some of the hydroxides, such as water, HOH, ethyl alcohol, C_2H_5OH, are neutral and again a large number of them such as sulphuric acid, $SO_2(OH)_2$, phosphoric acid, $PO(OH)_3$ and boric acid, $B(OH)_3$, are acidic. It has become customary to use the term hydroxide to hydroxy compounds which give basic

solutions or contain the hydroxly group as OH^- ion. The ionic oxides which react with water generally produce bases whereas the covalent oxides give acids.

In general, if the hydroxyl group exists in a compound as the OH^- ion, the compound is called a hydroxide. The hydroxides may be classified into various groups. The main groups of hydroxides are :—

I. Basic Hydroxides.
II. Amphoteric Hydroxides.
III. Acidic Hydroxides.
IV. Neutral Hydroxides.

I. Basic Hydroxides

Basic hydroxides are generally formed by metallic elements and the degree of electropositive character of the metal determines the basic properties and also the solubility of the basic hydroxides. Thus the alkali metal hydroxides are strongly basic and highly soluble in water and give high concentration of OH^- ions in solution. The alkaline earth metal hydroxides are less basic and less soluble in water as compared to the alkali metal hydroxides. The heavy metal hydroxides which are mostly insoluble in water are regarded as basic because they have the ability to react with acids to form salts and water. The relationship of the properties with the charge and size of the metal ions will be discussed latter. Thus, according to the properties, the basic hydroxides may be subdivided into three troups :—

(a) alkali metal hydroxides.

(b) Alkaline earth metal hydroxides.

(c) Heavy metal hydroxides.

The mode of formation of these three groups of basic hydroxides also illustrates the difference in their properties.

(a) Alkali metal hydroxides : (i) When an alkali metal comes in contact with water, there is a violent reaction, in course of which the alkali metal hydroxide is formed with evolution of hydrogen from water. The hydrogen burns in air with a flame indicating as if the alkali metal is burning in water.

$$2M + 2\,HOH \xrightarrow[\text{reaction}]{\text{violent}} 2\,MOH + H_2$$

(ii) When an alkali metal salt solution in water is electrolysed, the alkali metal is liberated at the cathode and reacts with water forming the hydroxides.

(iii) The alkali metal oxides are freely soluble in water to form alkali metal hydroxides in solution.

(iv) The alkali metal hydroxides are not converted to their oxides on strong heating.

(b) The alkaline earth metal hydroxides : (i) The reaction between water and the alkaline earth metal is not as violent as in the case of the alkali metals. As expected, the reactivity with water increases in the group with increasing atomic number. Lithium, an alkali metal, in this respect resembles magnesium as already explained in connection with the diagonal relationship in the Periodic Table.

$$M + 2\,HOH \xrightarrow[\text{reaction}]{\text{slow}} M\begin{matrix}OH\\OH\end{matrix} + H_2$$

(ii) The alkaline earth metal hydroxides are also formed by precipitation from their salt solutions by adding alkali hydroxides. Thus,

$$MgCl_2 + 2\,NaOH = Mg(OH)_2 + 2\,NaCl$$

(iii) The alkaline earth metal hydroxides are also formed by direct reaction of their oxides with water. thus,

$$CaO + H_2O = Ca(OH)_2$$

(iv) Unlike alkali metal hydroxides, the alkaline earth metal hydroxides are converted to their oxides on strong heating by loss of water. Thus,

$$Ca(OH)_2 \xrightarrow{-H_2O} CaO$$

$$Ba(OH)_2 \xrightarrow{-H_2O} BaO$$

(c) The heavy metal hydroxides : (i) The hydroxides of copper, nickel, iron cobalt etc. are included in this sub-group. The formations of these hydroxides do not take place with the direct reaction of the heavy metal, or their oxides with water. These hydroxides are best prepared by the addition of a soluble

alkali hydroxide to the heavy metal salt solutions in water. The heavy metal hydroxides are precipitated in the form of insoluble product :

$$FeCl_3 + 3\ NH_4OH = Fe(OH)_3 + 3\ NH_4Cl$$

$$CuSO_4 + 2\ NaOH = Cu(OH)_2 + Na_2SO_4$$

(ii) Since the heavy metal hydroxides are generally insoluble in water, their basic character is revealed by their dissolution in acids indicating neutralization reaction forming salts and water. Thus,

$$Fe(OH)_3 + 3\ HCl = FeCl_3 + 3\ H_2O$$

(iii) The heavy metal hydroxides are easily converted to their oxides by heating when water is lost. Thus,

$$Ni(OH)_2 \xrightarrow{-H_2O} NiO$$

It may be mentioned here that the results of the dehydration of a heavy metal hydroxide may produce intermediate products which may be described as oxyhydroxides. Some of these oxyhydroxides are formed during the direct reaction and no heating is required. However, on strong heating these oxyhydroxides also give the metallic oxides. Thus,

$$Fe(OH)_2 \xrightarrow[\text{dehydration}]{\text{Partial}} FeO.OH$$

$$Fe(OH)_2 \xrightarrow[\text{oxidation}]{\text{air}} FeO.OH \xrightarrow{\text{heating}} Fe_2O_3$$

$$Fe \xrightarrow[\text{or normal rusting}]{\text{Water vapour}} \underset{\text{Lepidocrocite}}{FeO.OH}$$

Similarly, MnO.OH, AlO.OH etc. are formed by partial dehydration of the normal hydroxides.

II. Amphoteric Hydroxides

In conformity with the definition of amphoteric oxides, the amphoteric hydroxides may be defined in a similar fashion since the latter are derived from the former. It is not possible to classify all hydroxides sharply as either basic or acidic. The hydroxides of those elements situated in the centre of the Periodic Table are amphoteric.

Amphoteric hydroxides are those which are able to neutralize both acids and bases and hence possess both acidic and basic characters.

For instance, $Be(OH)_2$, $Al(OH)_3$, $Zn(OH)_2$, $Pb(OH)_2$ etc. are amphoteric hydroxides and act both as acids or bases and hence are soluble in either strongly basic or strongly acidic solutions.

The acidic hydroxides generally give H^+ ions in solution and basic hydroxides produce OH^- ions as the case may be. Thus in the case of $Zn(OH)_2$, we have,

$$Zn(OH)_2 \longrightarrow Zn^{+2} + 2\,OH^- \text{ (basic)}$$

$$Zn(OH)_2 \longrightarrow ZnO_2^{-2} + 2H^+ \text{ (acidic)}$$

Hence, such hydroxides are soluble in acids, as in HCl and also in alkali, *e.g.* NaOH :

$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O$$

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$

A more precise equation showing the amphoteric behaviour of $Al(OH)_3$ may be given as follows :—

$$Al(OH)_3\,(H_2O)_3 + OH^- \rightleftharpoons Al\,(H_2O)_2\,(OH)_4^- + H_2O \;..\;(1)$$

$$Al(OH)_3\,(H_2O)_3 + H_3O^+ \rightleftharpoons Al\,(H_2O)_4\,(OH)_2^+ + H_2O \;..\;(2)$$

In equation (1), a proton is transferred from $Al(OH)_3\,(H_2O)_3$ to OH^-. In equation (2), a proton is transferred from H_3O^+ to $Al\,(OH)_3\,(H_2O)_3$.

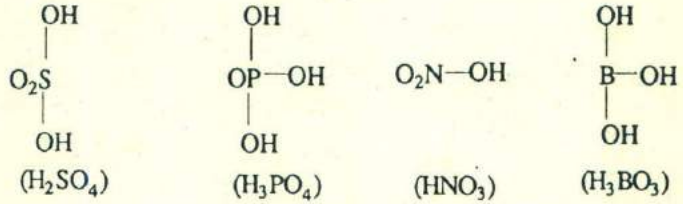
Similarly, for other amphoteric hydroxides the replacement of the surrounding groups of the metal as shown in the case of Al may be used to show the amphoteric character.

III. Acidic Hydroxides (Hydroxy Acids)

Both the metals and non-metals can form acidic hydroxides and definition follows the same pattern as that of the acidic oxides. But the acidic hydroxides of the non-metals are more important since they behave as strong acids.

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The acidic hydroxides are those which react with base to neutralize it producing salt and water :



From the above examples, we can derive a definition for the basicity of an acid.

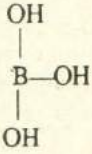
Basicity of an acid is the number of OH groups combined with an element and capable of producing H^+ ions. The basicity of the acids have been given in Table 8·2.

Table 8.2. Basicity of some acids.

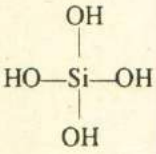
Acid	*Hydroxide form*	*Basicity*
H_2SO_4	$SO_2(OH)_2$	2
H_3PO_4	$PO(OH)_3$	3
HNO_3	$NO_2(OH)$	1
H_3BO_3	$B(OH)_3$	3
H_2SO_3	$SO(OH)_2$	2
$HClO_3$	$ClO_2(OH)$	1
$HMnO_4$	$MnO_3(OH)$	1
H_3AsO_4	$AsO(OH)_3$	3
H_3AsO_3	$As(OH)_3$	3
H_3PO_3	$POH(OH)_2$	2
H_3PO_2	$POH_2(OH)$	1
CH_3COOH	$CH_3CO(OH)$	1

Thus the acidic hydroxides contain one or more OH groups which are capable of producing H^+ ions by rupture of the O—H bond. The hydroxy acids are classified as ortho, meta- and pyro- acids on the basis of the OH groups and their elimination during condensation reaction.

Ortho-acids : Theoretically the fully hydroxylated compounds from the valence considerations are generally known as ortho-acids. Thus,



Orthoboric acid



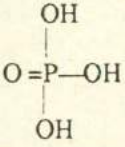
Orthosilicic acid

But in many cases the theoretical hydroxylated compounds are not formed or do not exist. The formula for the true orthocompounds may be written but these refer to only hypothetical compounds. Thus, ortho-phosphoric acid should be formed by the hydroxylation of P_2O_5 where all the 5 oxygen is replaced by OH :

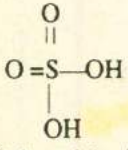
$$P_2O_5 \rightarrow P_2(OH)_{10} \quad \text{or} \quad P(OH)_5$$

Hypothetical ortho-phosphoric acid

But $P(OH)_5$ does not exist. Hence the compounds which contain the maximum number of OH groups in actual practice are generally referred to as ortho-acids. For instance,



Ortho-phosphoric acid



Ortho-sulphuric acid

Meta-acids : The meta-acids result from the ortho-acids. When water molecule is eliminated from one molecule of the ortho–compound, the product obtained is called a meta-acid. Thus,

$$\underset{\text{Ortho-phosphoric acid}}{OP(OH_3)} \xrightarrow{-H_2O} \underset{\text{Meta-phosphoric acid}}{O_2P(OH)} \quad \text{or} \quad HPO_3$$

$$\underset{\text{Orthoboric acid}}{B(OH)_3} \xrightarrow{-H_2O} \underset{\text{Metaboric acid}}{OB(OH)} \quad \text{or} \quad HBO_2$$

$$\underset{\text{Orthosilicic acid}}{Si(OH)_4} \xrightarrow{-H_2O} \underset{\text{Metasilicic acid}}{OSi(OH)_2} \quad \text{or} \quad H_2SiO_3$$

The meta-acids may also be derived from the hypothetical hydroxylated ortho-acids. Some of these compounds may give a series of meta-acids which may or may not exist. Thus fully hydroxylated ortho-acid of the compounds Cl_2O_7 may be formulated as given below. Thus, by elimination of one molecule of H_2O successively, gives rise to 1st-, 2nd-and 3rd meta-chloric acids.

$$\underset{\text{Hypothetical orthochloric acid}}{Cl(OH)_7} \xrightarrow{-H_2O} OCl(OH)_5$$

$OCl(OH)_5$ $\xrightarrow{\text{1st meta-}}$ $O_2Cl(OH)_3$ $\xrightarrow{\text{2nd meta-}}$ $O_3Cl(OH)$ $\xleftarrow{-H_2O}$ $O_3Cl(OH)$

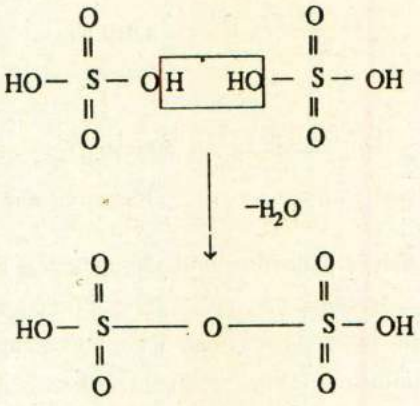
3rd meta-(Perchloric acid)

Pyro-acids : Pyro-acids are formed when two or more molecules of the true ortho-or any intermediate form or meta-acids combine together with the elimination of water molecule. The pyro-acids are formed by condensation reaction and the compounds formed are also known as condensed products. Thus, two molecules of orthophosphoric acid may combine by elimination of 1 molecule of H_2O to form pyrophosphoric acid.

$$\underset{\text{Orthophosphoric acid (two molecules)}}{OP(OH)_3 + OP(OH)_3} \xrightarrow{-H_2O} O_3P_2(OH)_4 \quad \text{or} \quad \underset{\text{Pyrophosphoric acid}}{H_4P_2O_7}$$

$$\underset{\text{4 molecules of } H_3BO_3}{4\ B(OH)_3} \xrightarrow{-5H_2O} O_5B_4(OH)_2 \text{ or } H_2B_4O_7$$

Pyroboric acid $H_2B_4O_7$



pyrosulphuric acid or $H_2S_2O_7$

IV. Neutral Hydroxides

These hydroxides do not ordinarily show acidic or basic behaviour, and neither form H^+ or OH^- ions, although both the groups may be present in the molecular structures. The organic hydroxy compounds, Such as alcohols like CH_3OH, C_2H_5OH etc. have OH group which does not give H^+ or OH^- ions and hence are neutral. Similarly, water. HOH, is neutral.

Acidic and Basic Character of Hydroxides

It may generally be concluded that an OH group present in an acid, ionizes to form a H^+ ion. But an OH group present in a metal hydroxide produces an OH^- ion. This necessarily implies that a hydroxy compound or hydroxide having the general formula MOH, behaves as an acid or as a base or as neutral according to the nature of the bonding in OH group. If the OH bond is ruptured or undergoes a *cleavage* in such a manner as to produce H^+ ion, the compound is an acid; and if the cleavage occurs to give OH^- ion, the compound is a base. A hydroxy compound MOH may undergo cleavage as in (I) or (II).

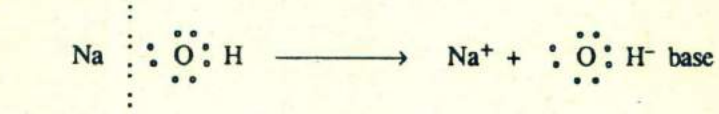


(I)



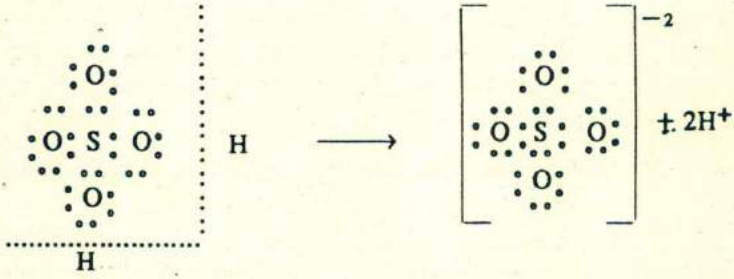
(II)

Thus in (I) the rupture takes place so that the electron pair is retained by the oxygen atom and the ions M^+ and OH^- are formed. This cleavage gives a base. In (II), the electron pair is retained by the oxygen atom together with the element M, forming an MO^- ion and H^+ ion. This cleavage gives an acid. If the bond is such that no cleavage of the above type occurs, the hydroxide will behave as a neutral substance. If M has very low electronegativity, the electrons are shifted towards oxygen and away from M. Thus NaOH gives Na^+ and OH^- ions



But if M is a highly electronegative non-metal, such as Cl, the electrons are pulled towards the Cl, away from H. Withdrawal of electron from H to O and finally the increase of electron density towards M, will leave H to be ionized as H^+ ion and MO group as negative MO^- ion. Such substances act as acid.

H_2SO_4 having the electronic structure shown below behaves as an acid because of the shifting of electron density away from H atoms for the same reason :



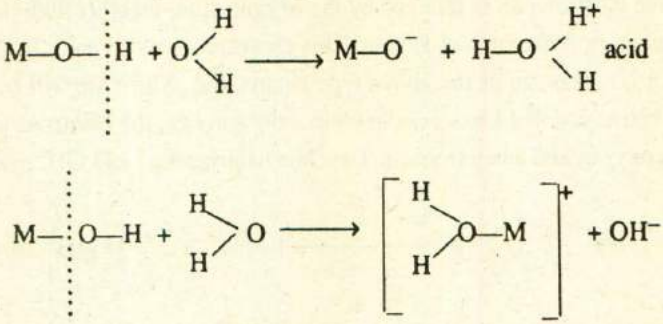
The general equation of the dissociation of a hydroxide may thus be represented by the following equations :

$$M(OH) \longrightarrow M^+ + (OH)^- \text{ base}$$

$$M(OH) \longrightarrow MO^- + H^+ \text{ acid}$$

or generally,

$M(OH)_n \rightleftharpoons M^{+n} + n(OH)^-$ and $M(OH)_n \rightleftharpoons MO_n^{-n} + nH^+$ The two ways in which hydroxides may react with H_2O are as follows :



If M—O bond is almost covalent, then O—H bond in the hydroxide is broken giving H^+ (H_3O^+) ion and hence acidic. If M—O bond is ionic, water tends to attack M, displacing the OH^- ion and giving basic reaction with the formation of hydrated ion $[M—H_2O]^+$. It may also be mentioned that those cations that become attached to the oxygen of H_2O, break the O—H bond releasing H^+ ion and are thus acidic. The anions that attack the H of H_2O, dislodge the OH^- ion and are basic. Thus Hg^{+2}, Cu^{+2} are acidic; C_2^{-2}, NH_2^- and S^{-2} are basic. These reactions are known as "hydrolysis" to which reference has already been made earlier.

The hydroxyl compounds of metals, which have various oxidation states, become less basic and more acidic as the oxidation state is increased. For instance, the hydroxides of manganese exhibit marked difference in acid-base behaviour as shown in Table 8.3.

Table 8.3. Acid-base character of hydroxides and oxidation states of Mn.

Compound	*Hydroxide formulation*	*Oxidation state*	*Character*
$Mn(OH)_2$	$Mn(OH)_2$	Mn(+2)	moderately basic
$Mn(OH)_3$	$Mn(OH)_3$	Mn(+3)	Weakly basic
H_2MnO_3	$MnO(OH)_2$	Mn(+4)	Weakly acidic
H_2MnO_4	$MnO_2(OH)_2$	Mn(+6)	Definitely acidic
$HMnO_4$	$MnO_3(OH)$	Mn(+ 7)	Strongly acidic

Manganese in its +2 state behaves as a typical metal giving the basic hydroxide $Mn(OH)_2$. But in permanganic acid Mn has oxidation state +7 and shows a non-metallic character analogous to chlorine In $HClO_4$. This may be viewed from the positions of both Mn and Cl in the Periodic Table since both occupy group VII, although Mn is a transition element. The high charge of Mn (+7) strongly attracts electrons. The O—H bonds in H_2O become very weak and protons are split off to leave the oxygen associated with Mn. Thus $HMnO_4$ behaves as a strong acid in water.

Questions and Problems

1. What are the different classes of oxides ? Discuss their properties and reactions.
2. Why is $Mg(OH)_2$ formed when magnesium reacts with water whereas MgO is produced when it burns in steam?
3. Arrange the following oxides in the order of increasing acidity:—
   As_2O_3, B_2O_3, BaO, BeO, FeO, N_2O_5, P_2O_4, P_2O_3, Cl_2O_7.
4. Write an equation showing that H_2O_2 is an acid.
5. Distinguish between dioxides and peroxides in terms of electronic structures.
6. How will you classify peroxides on the basis of their reactions and on the basis of their structures? Illustrate your answer with examples.
7. What are peroxides, superoxides and polyoxides? How will you distinguish them from one another?
8. What is meant by the basicity of an acid? Give examples.
9. Define with examples ortho-, meta- and pyro-acids. Discuss the modes of formation of meta-acid and pyro-acid from ortho-acids.
10. Discuss the amphoteric character of hydroxides.
11. What is the relationship between the oxidation states and the acidic and basic character of metal hydroxides?
12. How will you classify the oxides in terms of bonding systems? Give examples.
13. Predict the product in the following reactions:—
    (a) A few drops of hot water are added to solid sodium peroxide.
    (b) Sodium peroxide is dissolved in excess cold water.
    (c) Potassium superoxide and manganese dioxide are added to dilute H_2SO_4.
    (d) SO_3 is added to H_2O_2.
    (e) SO_3 gas is passed over CaO.

14. Explain peroxides with examples.
15. Describe the preparation. properties and uses of sulphur trioxide, nitrogen tetroxide.
16. How is orthophosphoric acid converted to other phosphoric acids?
17. Write the acidic and basic characters of oxides.
18. Write a note on modern views of acids and bases.
19. Explain why H_2O is neutral, HOCl is acidic and NaOH is alkaline.
20. What are amphoteric oxides?
21. Classify the following as acidic, basic, amphoteric or neutral oxides :—
    SO_2, $C_{r2}O_3$, P_4O_{10}, BeO, CO_2
22. Comment on the acidic and basic character of the following oxides :—
    MnO, MnO_2, Mn_2O_3, Mn_2O_7, Mn_3O_4
23. Non-metal oxides create air pollution problems. Explain the reasons.
24. How would you distinguish between peroxides and super oxides ? Give examples of their reactions.

CHAPTER 9

ACIDS AND BASES

The acids and bases are among the most important classes of compounds and these two classes of substances are, in effect, opposite to each other and yet interrelated through neutralization reactions forming salts which, therefore, become closely related to acids and bases. It may be mentioned that the terms *acids* and *bases* have been defined in many ways according to various concepts. In this chapter a brief review of some of the elementary concepts regarding acids and bases are given.

1. The Arrhenius Concept

According to Arrhenius concept an acid is a hydrogen-containing substance which yields H^+ ion (i.e., H_3O^+, hydronium ion) when dissolved in water.

Base is a substance which contains OH groups and produces OH^- ion when dissolved in water.

Arrhenius concept is based upon ionic dissociation of compound in water. Thus HCl is an acid because it produces H_3O^+ ion in water but CH_4 is not an acid. Similarly, NaOH is a base because it yields OH^- ion in water but C_2H_5OH is not a base. CH_4 does not yield H^+ ion in water, so also C_2H_5OH does not give OH^- ion in water :

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$NaOH + H_2O \longrightarrow Na^+ + OH^-$$

The strengths of acids and bases according to the Arrhenius concept are defined in terms of the concentrations of H^+ ion and OH^- ion respectively that are present in aqueous solution.

The process of neutralization is, therefore, considered to be the combination of H^+ ions and OH^- ions to form neutral water :

$$H^+ + OH^- \longrightarrow H_2O$$

The above definitions for acids, bases and acid-base reactions have been extended to apply to more general cases by several new concepts.

2. The Protonic or Brönsted Concept

According to Brönsted concept, also known as Brönsted-Lowry concept, the following definitions for acids and bases have been adopted as a modification of the Arrhenius concept.

An acid is a substance that can give up protons to another species.

A base is a substance that can accept protons.

Stated more simply, an acid is a proton donor, while a base is a proton acceptor.

It can be seen that the Brönsted concept does not specify a solvent. Acids and bases are related by the general equation :

$$\underset{\text{acid}}{HB} \longrightarrow \underset{\text{proton}}{H^+} + \underset{\text{base}}{B^-}$$

Generally, it may be written as

$$\text{Acid} \rightleftharpoons \text{Base} + \text{Proton}$$

For instance, when ammonia in dissolved in water, the reaction

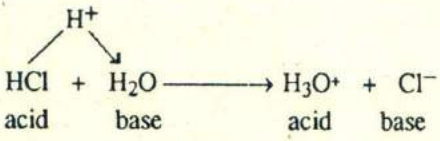
$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

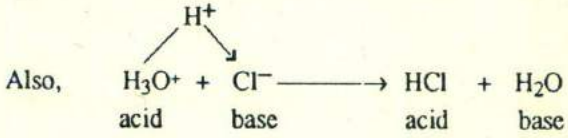
takes place. Here H_2O gives up the proton and is an acid and NH_3 accepts the proton and is, therefore, a base. Similarly, the reverse reaction indicates NH_4^+ as an acid and OH^- as a base. Thus in the above reaction, two acids and two bases are involved at equilibrium conditions. The acid-base pair associated with the loss or gain of proton is called a *Conjugate Pair*. Thus, NH_4^+ is the conjugate acid of the base NH_3 and H_2O is the conjugate acid of base OH^- and vice versa. The general equation for the equilibrium reaction may be written as

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1$$

Thus, in order that an acid acts as a proton donor, a proton acceptor must be present to receive it. The ions which remain after protons have been donated from the acid molecule are the *Conjugate bases* of the respective acid. Similarly,

the species formed when a proton is added to a base is the *Conjugate acid* of that base.





Some of the acid-base systems according to the Brönsted concept are given below :

$Acid_1$		$Base_2$		$Acid_2$		$Base_1$
HCl	+	NH_3	⟶	NH_4^+	+	Cl^-
NH_4^+	+	OH^-	⟶	H_2O	+	NH_3
H_3O^+	+	OH^-	⟶	H_2O	+	H_2O
H_2O	+	NH_3	⟶	NH_4^+	+	OH^-
HSO_4^-	+	OH^-	⟶	H_2O	+	SO_4^{-2}

Thus, Cl^-, SO_4^{-2}, OH^- are conjugate bases of HCl, HSO_4^- and H_2O respectively. H_2O, HSO_4^- and HCl are conjugate acids of the bases OH^-, SO_4^{-2} and Cl^- respectively.

Thus, the following species may be regarded as acids :—

Molecular species : HCl, H_2SO_4, CH_3COOH, HCN, H_2S, H_2O etc.

Anionic species : HSO_4^-, HCO_3^-, $H_2PO_4^-$, HPO_4^{-2}, HS^- etc.

Cationic species : H_3O^+, NH_4^+, $Al(H_2O)_6^{+3}$ etc.

The following species are regarded as bases :—

Molecular species : H_2O, NH_3, CH_3NH_2 etc.

Anionic species : OH^-, HS^-, S^{-2}, HCO_3^-, HSO_4^-, Cl^- etc.

Cationic species : $Fe(H_2O)_5OH^{+2}$, $Cu(H_2O)_3OH^+$ etc.

From the above examples of acids and bases, it is seen that certain species are classed as both acids and bases depending upon the manner they behave in a given reaction.

Amphiprotic species : A species that acts both as a proton donor and proton acceptor is said to be amphiprotic.

Thus, H_2O is amphiprotic. It loses proton to a base, such as NH_3, or accepts a proton from an acid, such as HCl :

$$\underset{\text{acid}}{H_2O} + \underset{\text{base}}{NH_3} \longrightarrow NH_4^+ + OH^-$$

$$\underset{\text{base}}{H_2O} + \underset{\text{acid}}{HCl} \longrightarrow H_3O^+ + Cl^-$$

Hence neutralization reactions according to Brönsted concept are acid-base reactions between the conjugate acid and conjugate base of an amphiprotic solvent.

The proton-containing negative ions are amphiprotic;

$$\underset{\text{acid}}{HS^-} + \underset{\text{base}}{OH^-} \longrightarrow S^{-2} + H_2O$$

$$\underset{\text{base}}{HS^-} + \underset{\text{acid}}{H_3O^+} \longrightarrow H_2S + H_2O$$

The conjugate base and acid relationship may be shown as :

$-H^+$ ↗ OH^- Conjugate base of water
H_2O
$+H^+$ ↘ H_3O^+ Conjugate acid of water

$-H^+$ ↗ CO_3^{-2} Conjugate base of HCO_3^-
HCO_3^-
$+H^+$ ↘ H_2CO_3 Conjugate acid of HCO_3^-

Amphoteric hydroxides react with both acids and bases because they are generally amphiprotic :

$$\underset{\text{acid}}{[Al(H_2O)_3(OH)_3]} + \underset{\text{base}}{OH^-} \longrightarrow [Al(H_2O)_2(OH)_4]^- + H_2O$$

$$\underset{\text{base}}{[Al(H_2O)_3(OH)_3]} + \underset{\text{acid}}{H_3O^+} \longrightarrow [Al(H_2O)_4(OH)_2]^+ + H_2O$$

According to Brönsted concept a solution of NaCl in H_2O is neutral, since Na^+ and Cl^- do not exhibit any tendency to gain proton in H_2O which is the solvent and in which NaCl is not hydrolysed. But aqueous solutions of $AlCl_3$, $ZnCl_2$ and $FeCl_3$ etc. show acidic reactions because the cations are hydrated and hydrolysed. Thus, Al^{+3} ion is hydrated $[Al(H_2O)_6]^{+3}$ and hydrolysed as indicated above. $[Al(H_2O)_6]^{+3}$ is an acid and donates a proton to H_2O, which acts as a base. The enhanced proton releasing tendency of Al^{+3} ion is due to the co-ordination of H_2O to Al^{+3} in which the electrons are shifted towards the positi-

$$Al^{+3} \longleftarrow :O\begin{matrix}H\\H\end{matrix}$$

vely charged Al^{+3}, thereby weakening the O—H bond. H^+ ion is thus released easily. Generally, small ions with high positive charge become hydrated in aqueous solution and act as Brönsted Acids. Na^+, K^+ etc. which are of large size and small charge do not show this character.

Polyprotic acid : Acids containing one proton which can be donated is *monoprotic acid*. Those acids containing more than one donatable proton are known as *polyprotic acids*. Thus HCl, HNO_3, HCN etc. are monoprotic, whereas H_3PO_4, H_2SO_4, H_3AsO_4 are polyprotic.

Non-aqueous system : Non-aqueous solutions also lose or gain proton and fit into the Brönsted concept of acids and bases. Thus when water is dissolved in liquid ammonia :

$$\underset{\text{acid}}{H_2O} + \underset{\text{base}}{NH_3} \longrightarrow NH_4^+ + OH^-$$

When perchloric acid is dissolved in concentrated H_2SO_4, acid-base reaction occurs :

$$\underset{\text{acid}}{HClO_4} + \underset{\text{base}}{H_2SO_4} \longrightarrow H_3SO_4^+ + ClO^-_4$$

When concentrated H_2SO_4 is dissolved in glacial acetic acid, we have again acid-base reaction :

$$\underset{\text{acid}}{H_2SO_4} + \underset{\text{base}}{CH_3COOH} \longrightarrow HSO_4^- + CH_3COOH_2^+$$

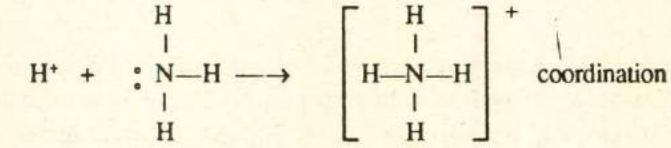
3. The Lewis Concept

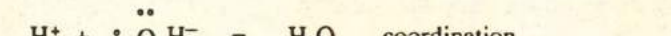
G. N. Lewis has proposed a more generalized theory in which acids and bases have been defined on the basis of electronic structures.

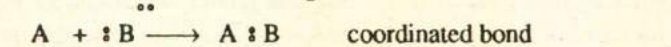
An acid is a substance (molecules or ions) which can accept a pair of electrons.

A base is a substance (molecules or ions) which can donate a pair of electrons.

An acid-base reaction, therefore, consists of the donation of a pair of electrons from a base to an acid with the formation of a coordinate bond between the two.

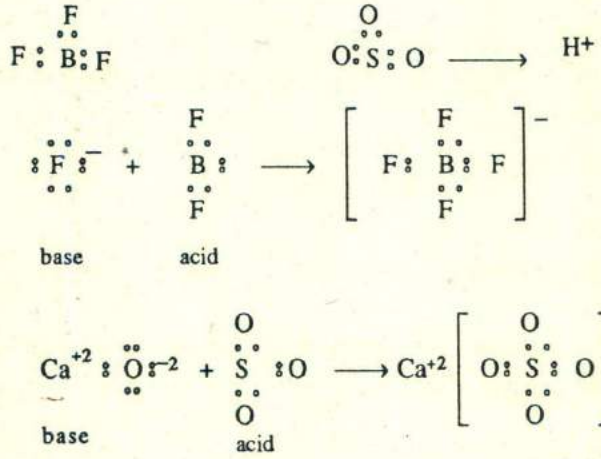






From the electronic configurations, different types of Lewis acids may be distinguished.

(i) Compounds having less than a full octet of electrons, e.g., BF_3 and SO_3 :



(ii) Positive ions are often considered as acids :

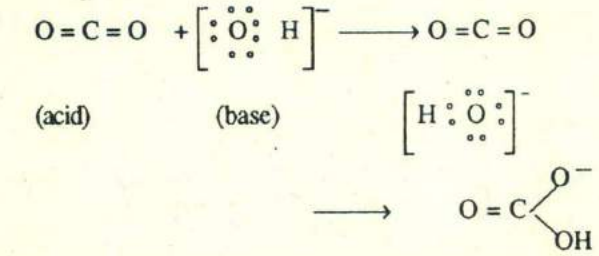
$$Ag^{+} + 2\,{:}NH_3 \longrightarrow [Ag({:}NH_3)_2]^{+}$$
acid base

$$Co^{+3} + 6NH_3 \longrightarrow [Co({:}NH_3)_6]^{+3}$$
acid base

(iii) Metal atoms, such as Ni, function as an acid in the formation of nickel carbonyl :

$$Ni + 4\,{:}CO \longrightarrow Ni(CO)_4$$

(iv) Compounds having double or multiple bonds (except C=C double bond). These have acidic sites :



$$SO_2 + O^{-2} \longrightarrow \left[O \overset{O}{\underset{S}{}} O\right]^{-2}$$

(v) Compounds having the central atom capable of expanding its valence shell are Lewis acids :

$$SnCl_4 + 2Cl^- \longrightarrow [SnCl_6]^{-2}$$

$$SiF_4 + 2F^- \longrightarrow [SiF_6]^{-2}$$

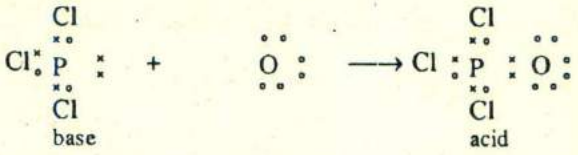
$$PCl_5 + Cl^- \longrightarrow [PCl_6]^-$$

Since Lewis acids draw electron towards it, they are known as "*electrophilic* (electron loving) reagents.

Lewis bases can also be grouped as follows :—

(i) Molecules containing an atom with two or less number of unshared electron-pairs. Thus the number of unshared electron-pairs in Ne, HF, H_2O, NH_3, PCl_3 etc. determines the properties and the reactions.

Atom or molecule	*Electronic structure*	*No. of paired electrons (lone pairs)*	*Reaction*	*Example*
Ne	:Ne:	4	Non-basic	×
HF	H:F:	3	Very weakly basic	$HF + :SO_3 = HF:SO_3$
H_2O	H—O: (H)	2	basic	$H_2O:H^+$
NH_3	H—N: (H, H)	1	Strongly basic	$H_3N:BF_3$



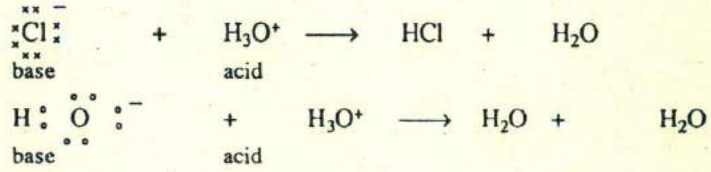
Base strength decreases in the series :

$CH_3N > H_3N > F_3N$— Electron with charge capacity different.

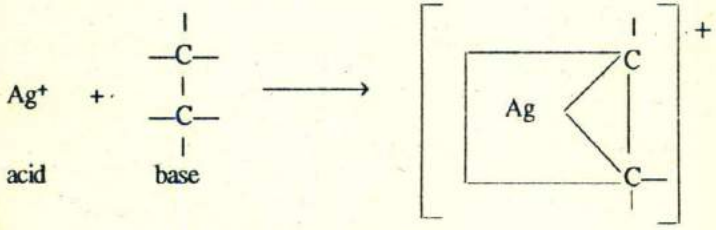
Acid strength decreases in the series :

$BBr_3 > BCl_3 > BF_3$ — because of greater resonance stabilization.

(ii) Negative ions are Lewis bases :



(iii) Compounds containing C=C double bonds also act as Lewis bases. High solubility of $AgClO_4$ in benzene is considered as an acid-base reaction on the basis of Lewis concept. Interactions of —C=C— with BF_3, $AlBr_3$ etc. also represent acid-base reactions. Ag^+ ion with hydrocarbon gives "π-complex". Interactions of $AlCl_3$ and BF_3 with —C = C— also result in the formation of "π-complexes".



$AlCl_3 + Cl^- \longrightarrow [AlCl_4]^-$

acid base

Lewis bases supply electron pair to a nucleus and are "*nucleophilic* (nucleus loving) reagents".

4. The Lux-Flood Concept

Protonic concept of Bronsted cannot be applied to systems having no proton particularly in the case of oxide systems. According to Lux-Flood concept, the definitions of acids and bases are as follows :—

Base : Any substance which gives up oxide ion (O^{-2}).

Acid : Any substance which gains or takes up oxide ions.

Hence,

$$\text{base} \rightleftharpoons \text{acid} + nO^{-2}$$

This view is particularly applicable to reaction at high temperature.

CaO is a base because it gives up O^{-2} ions :

$$\underset{\text{base}}{CaO} \rightleftharpoons \underset{\text{acid}}{Ca^{+2}} + O^{-2}$$

SO_4^{-2} is a base because it gives up O^{-2} ions :

$$SO_4^{-2} \rightleftharpoons SO_3 + O^{-2}$$

$$\underset{\text{base}}{CaO} + \underset{\text{acid}}{SO_3} \xrightarrow{\Delta} \underset{\text{acid}}{Ca^{+2}} + \underset{\text{base}}{SO_4^{-2}}$$

$$\underset{\text{base}}{CaSO_4} + \underset{\text{acid}}{SiO_2} \longrightarrow \underset{\text{acid}}{Ca^{+2}} + \underset{\text{base}}{SiO_3^{-2}} + \underset{\text{acid}}{SO_3}$$

SO_3 and Ca^{+2} are acids because they take up oxide ions as shown by the above equation :

$$\underset{\text{acid}}{SO_3} + \underset{\text{base}}{ZnO} \xrightarrow{\Delta} ZnSO_4$$

$$\underset{\text{base}}{Na_2O} + \underset{\text{acid}}{ZnO} \xrightarrow{\Delta} 2Na^{+} + ZnO_2^{-2}$$

Strength of acids is determined by the magnitude of the equilibrium constant,

$$K = \frac{[Acid] \times [O^{-2}]}{[base]}$$

According to this concept, the strength of the following acids are given in the increasing order :

$$PO_4^{-3} > BO_2^{-} > SiO_3^{-2} > TiO_3^{-2}$$

5. The Usanovich Concept

This concept gives a comprehensive definition of acids and bases comprising all aspects of their reactions.

An acid in defined as any substance which—

(i) neutralizes a base,
(ii) gives up cations,
(iii) combines with anions or electrons.

Similarly, a base is defined as any substance which—

(i) neutralizes an acid,
(ii) gives up anions or electrons,
(iii) combines with cations.

The following examples in a tabular form explain the various aspects of the Usanovich concept :—

Acid	*Base*	*Salt*	*Justification*
SO_3	Na_2O	Na_2SO_4	Na_2O gives O^{-2}
			SO_3 combines with O^{-2}
$Fe(CN)_2$	KCN	$K_4Fe(CN)_6$	KCN gives CN^-
			$Fe(CN)_2$ combines with CN^-
Sb_2S_3	$(NH_4)_2S$	$(NH_4)_2SbS_4$	$(NH_4)_2S$ gives S^{-2}
			Sb_2S_3 gains S^{-2}
Cl_2	Na	NaCl	Na loses an electron
			Cl gains an electron
HCl	NH_3	NH_4Cl	HCl gives H^+
			NH_3 combines with H^+
NH_4^+	OH^-	$NH_3 + H_2O$	NH_4^+ gives H^+
			OH^- combines with H^+

The Strengths of Acids

From the point of view of ionization theory, the strengths of acids (or bases) depend on the extent to which they dissociate into ions.

As mentioned in chapter 8, a molecule represented by MOH dissociate giving an OH^- or H^+ ions depending on the charge and size and electronegativity of M. A large ion with a small positive charge has less attraction for the electron of the OH^- ion than does a small ion with a positive charge.

Thus alkali metal hydroxides, MOH, form strong bases and their strength increases as the size of the alkali metal ion increases. The comparative strengths of the various bases are qualitatively given in Table 9.1.

Table 9.1. Strengths of bases on the basis of ion size and charge of the metals.

Base	*Size of the metal ion* Å	*Charge of metal ion*	*Qualitative strengths*
LiOH	0.60	+1	Weak base
NaOH	0.95	+1	Strong base
KOH	1.33	+1	Very strong base
CsOH	1.69	+1	Strongest base
$Mg(OH)_2$	0.65	+2	Weaker base
$Al(OH)_3$	0.50	+3	Weaker base (Amphoteric)

The strength of an acid is a measure of tendency of its conjugate base to part away with the proton to another base. A strong acid having a great tendency to donate proton is a conjuate to weak base with small tendency to accept proton. Hence stronger the acid the weaker is the conjugate base and stronger the base the weaker is the conjugate acid. Thus, strong HCl has a weak conjugate base Cl^-. The polyprotic acids, such as H_3PO_4, undergo stepwise ionization reactions. The strength in this case can be measured by ionization constants K. Thus the smaller the value of ionization constant K, the less is the degree of ionization and hence less strong the acid. This applies to other polyprotic acids and provides an approximate measure of the relative strengths of acidity due to ionization. The neutral molecule more readily gives up the proton than does the negatively

charged anion. The strength of an acid depends mainly upon the value of the first ionization constant.

$$H_3PO_4 \rightleftharpoons H^{+1} + H_2PO_4^{-1} \qquad K_1 = 0.75 \times 10^{-2}$$

$$H_2PO_4^{-1} \rightleftharpoons H^{+1} + HPO_4^{-2} \qquad K_2 = 0.62 \times 10^{-7}$$

$$HPO_4^{-2} \rightleftharpoons H^{+1} + PO_4^{-3} \qquad K_3 = 1 \times 10^{-13}$$

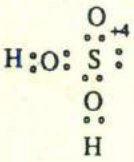
$$\text{Where } K_1 = \frac{[H^+]\,[H_2PO_4^{-1}]}{[H_3PO_4]} \text{ and so on for } K_2 \text{ and } K_3.$$

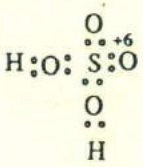
Thus the smaller the value of ionization constant K, the less is the degree of ionization and hence less strong the acid.

Comparing the electronic structure of some acids and the first ionization constants it is found that the oxidation number of the central atom determines the strengths of the acids. Thus, H_2SO_4 is a stronger acid than H_2SO_3 or H_3PO_4 because the oxidation number of S in H_2SO_4 is +6 and in H_2SO_3 it is +4 and that of P in H_3PO_4 is +5. Thus,

$\overset{+6}{H_2SO_4}$ $\qquad$ $\overset{+5}{H_3PO_4}$ $\qquad$ $\overset{+4}{H_2SO_3}$

S with oxidation number +6 in H_2SO_4 obviously exerts a greater pull on all the electron pairs of O atoms than does S in H_2SO_3 :





The comparative strengths of some well-known hydroxy acids (oxyacids) on the basis of the oxidation numbers of the acid-forming elements are given by the sequence:

$$\overset{7}{HClO_4} > \overset{6}{H_2SO_4} > \overset{5}{HNO_3} > \overset{4}{H_2SO_3} > \overset{3}{H_3AsO_3} > \overset{1}{HClO}$$

Both the charge and the size of the central element determine the strengths of the acids in the above compounds. For instance,

$$\overset{4}{H_2SO_3} > \overset{4}{H_2SeO_3}$$

because of the smaller size of S than Se although the oxidation number is the same in both cases.

Ionic Potential : The ratio between the charge and the radius of an ion is called ionic potential. If Z is the charge, r the radius of an ion, then the ionic potential φ is expressed as,

$$\varphi = \frac{Z}{r}$$

It has been shown that values of φ also determine the acidic or basic character of a compound or an ion. Thus,

$\sqrt{\varphi} > 3.2$ — acidic

$\sqrt{\varphi} < 2.3$ — basic

$2.3. < \sqrt{\varphi} < 3.2$ — amphoteric

The strengths of acids may be correlated to the number of oxygen and hydrogen atoms in the molecule in two ways :—

(1) The greater the difference between the number of oxygen and number of hydrogen atoms, the stronger the acid.

(2) The greater the number of non-hydrogenated oxygen atoms per molecule, the greater is the strength of acid.

These two points have been illustrated in the Table 9.2 regarding oxyacid of the general formula

$$H_xMO_y$$

where x and y are the numbers of hydrogen and oxygen atoms in the molecule respectively.

In the cases of acids which do not contain the oxygen atoms, the determination of strengths is based mainly on the ionic sizes or interatomic distance or electronegativity of H and the non-metallic element forming the acid molecule. Thus, the following two series have been arranged in decreasing acidity :

$$HF > H_2O > NH_3$$
$$HI > HBr > HCl > HF$$
$$H_2Te > H_2Se > H_2S > H_2O$$

The decreasing electronegativity in the order F > O > N gives rise to decreasing strengths of acids. But the decreasing atomic sizes of halogens and those in the chalcogens series produce acids of decreasing strengths. In the halogen acids, the bond distances H—X increase from 1.0 Å for HF to 1.7 Å in HI and also the bond energy decreases. HI, therefore, is a stronger acid since it gives up proton relatively easily. The charge of the anion also influences base strengths. For instance, the base strength of the monoatomic anions increases in the series $N^{-3} > O^{-2} > F^-$, i.e., NH_3 is a stronger base than H_2O which is a stronger base than HF.

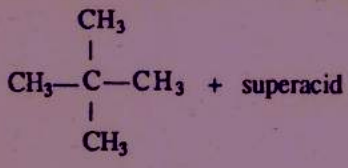
In the case of oxyacids the factors influencing the acid strengths are : (i) electronegativity, (ii) number of oxygen atoms and (iii) the oxidation state of the element forming the hydroxy compounds. These are shown in Table 9.2.

Superacids : When strong acids are dissolved in very acidic solvents, the solutions are highly effective protonating agents. Such solutions are known as *superacids*. Fluorosulphonic acid and hydrogen fluoride act as good systems for the formation of superacids :

$$SbF_5 + HF \longrightarrow SbF_6^- + H_2F^+$$

$$SbF_5 + HSO_3F \longrightarrow FSO_3SbF_5^- + H_2SO_3F^+$$

Alkanes are easily protonated by superacids :



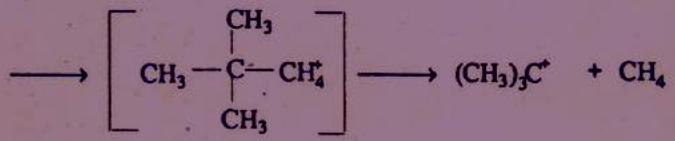


Table 9.2. Relative strengths of oxyacids of the general formula HxMOy.

Acid	*Structural formula*	*No. of H atoms x*	*No. of O atoms y*	*y—x*	*No. of non-hydrogenated O atoms*	*First ionization constant (K)*	*Strengths of acid (Remarks)*
$\overset{+1}{HClO}$	Cl(OH)	1	1	0	0	9.6×10^{-7}	very weak
$\overset{+3}{HClO_2}$	ClO(OH)	1	2	1	1	1×10^{-2}	weak
$\overset{+5}{HClO_3}$	$ClO_2(OH)$	1	3	2	2	$\sim10^{3}$	strong
$\overset{+7}{HClO_4}$	$ClO_3(OH)$	1	4	3	3	$\sim10^{8}$	very strong
$\overset{+1}{HBrO}$	Br(OH)	1	1	0	0	2×10^{-2}	weak
$\overset{+1}{HIO}$	I(OH)	1	1	0	0	1×10^{-11}	very weak
$\overset{+3}{H_3BO_3}$	$B(OH)_3$	3	3	0	0	5×10^{-10}	very weak
$\overset{+3}{H_3AsO_3}$	$As(OH)_3$	3	3	0	0	6×10^{-10}	very weak
$\overset{+5}{H_3AsO_4}$	$AsO(OH)_3$	3	4	1	1	5×10^{-3}	weak
$\overset{+4}{H_4SiO_4}$	$Si(OH)_4$	4	4	0	0	1×10^{-10}	very weak
$\overset{+3}{HNO_2}$	NO(OH)	1	2	1	1	4.5×10^{-4}	weak
$\overset{+5}{HNO_3}$	$NO_2(OH)$	1	3	2	2	$\sim10^{3}$	strong
$\overset{+4}{H_2SO_3}$	$SO(OH)_2$	2	3	1	1	1.7×10^{-3}	weak
$\overset{+6}{H_2SO_4}$	$SO_2(OH)_2$	2	4	2	2	$\sim10^{3}$	strong
$\overset{+5}{H_3PO_4}$	$PO(OH)_3$	3	4	1	1	7.5×10^{-3}	weak
$\overset{+7}{HMnO_4}$	$MnO_3(OH)$	1	4	3	3	$\sim10^{8}$	very strong

Acids & base as catalysts :

1. $CH_3COOH + C_2H_5OH \xrightarrow[\text{Catalyst}]{H_2SO_4} CH_3COOC_2H_5 + H_2O.$

2. $C_6H_6 + CH_3Cl \xrightarrow[\text{Catalyst}]{AlCl_3} C_6H_5CH_3 + HCl.$

3. $RX + H_2O \xrightarrow[\text{Catalyst}]{\text{aq. KOH}} ROH + HX.$

Hard & Soft Acids and Bases (HSAB)

The classification is based on electronegativity values and size and is actually a form of Lewis acid-base concept.

Hard acids : These are metals having low electronegativity values usually 0.7 to 1.6. Exception is H^+ ion which is also a hard acid on the basis of very small size. Similarly ions such as B^{+3}, C^{+4} are hard acids because of very small size and high charge.

Hard Bases : Donor atoms of very high electronegativity values such as oxygen and flourine. The oxoanions such as SO_4^{-2}, CO_3^{-2}, PO_4^{-3} etc. are included in this group.

Soft Acids : Metals having high electronegativities (1.9 — 2.5) and also having large size and low charge are soft acids. Ag^+, Au^+, Pt^{+2}, Hg^{+2}, Pb^{+2} etc. are soft acids.

Soft Bases : Group of ligands containing non-metal electronegative elements such as C, P, As, Br, I and H^- ion (having electronegativity values 2.1 - 2.96 are included in soft acids.

The equilibrium of the reaction between Hard and Soft acids and bases generally follow the equation :

$$HA : SB + SA : HB \rightleftharpoons HA : HA + SA : SB$$

Applications of HSAB principle :

1. Qualitative analysis scheme for metal cations.
2. Oxidation reduction reactions.
3. Geochemical classification of elements and their occurrence in nature as minerals.

4. Toxicology of the elements and medicinal chemistry.
5. Clinical application and chelation therapy.

QUESTIONS AND PROBLEMS

1. Write a brief note on Brönsted concept of acids and bases.
2. Write a note on modern views about acids and bases.
3. Write a short note on Lewis concept of acids and bases.
4. Write a note on Lewis and Brönsted concepts of acids and bases.
5. What is the relationship of charge and size of the acid-forming elements with the strength of the acid?
6. Arrange the following acids in terms of increasing strength :—
   H_3BO_3, H_4SiO_4, HNO_2, HNO_3, H_2SO_4, $HMnO_4$.
7. What is the basis of the strength of acids in halogen acids?
8. How will you determine the strength of acids in terms of the oxidation number of the acid-forming elements?
9. What are amphiprotic substances ? Illustrate with suitable examples.
10. Define the terms "acid" and "base" according to the Arrhenius concept and the protonic concept.
11. Write equations for the reaction of the following acids with water :—
    HCl, HNO_3, $HClO_4$ and NH_4^+. What is the role played by water in these acid-base reactions?
12. Classify the following substances as acids and bases giving reasons:—
    BF_3, NH_3, NH_4^+, Ag^+, SO_3, CaO, KCN, OH^-, SO_4^{-2}, Na, Cl_2, H^+.
13. What are the conjugate acids and bases? What are the conjugate bases of the following acids?
    H_2CO_3, H_2O, $HClO_4$, HCN
14. Give a brief account of modern views regarding acids and bases.
15. Write a note on acids and bases.
16. Write a note on modern views on acids and bases.
17. What are hard and soft acids and bases? Mention about the applications of hard and soft acids and bases concept.

CHAPTER 10

THE ATMOSPHERE AND THE INERT GASES

The Composition of the Atmosphere

The atmosphere is the mixture of gases which surrounds the earth. A small portion of the atmosphere is called air although the distinction may not be well-marked. In ancient time air was considered to be an element. But in 1775, Lavoisier established that air is a mixture of nitrogen and oxygen together with other gases. Nitrogen, oxygen and a number of inert gases are present in the atmosphere besides carbondioxide, water vapour and dust. Traces of hydrogen, hydrogen sulphide, ammonia, oxides of nitrogen, sulphur dioxide and other gases are also present. The composition varies according to location on the earth's surface and altitude. The average composition of dry air at sea-level by volume is given in Table 10.1.

Table 10.1. Composition of the atmosphere.

Component	*Percent by volume*	*Remarks*
Nitrogen	77.16	
Oxygen	20.60	
Argon	0.94	
Carbondioxide	0.04	variable
Moisture	0.140	variable
Neon	0.0018	
Helium	0.0005	
Krypton	0.0001	
Xenon	0.000005	
Hydrogen	Traces	
Ozone	Traces	
Dust particles & other gases	Traces	variable

The percentage composition of dry and pure air does not vary much with location on the earth's surface or with altitude. However, density of air and pressure varies greatly with altitude. Thus, the average pressure of air at sea-level is 760 mm. Hg, but at 15000 feet it is about 400 mm. Hg, at 10 miles it is 40 mm. and at 30 miles altitude it is only 0.1 mm. Similarly, density of air decreases with altitude.

Detection of the Presence of Main Constituents of Air

(a) Oxygen

Oxygen can be detected by a number of chemical methods :—

(i) By burning a number of metals and non-metals in air, it is found that the oxides of the elements are formed. Thus, phosphorus burns in air to form P_2O_5. Similarly, when air is passed over heated copper, formation of CuO takes place.

(ii) When a jar filled with NO gas is exposed to air, reddish brown fumes of NO_2 is formed showing the presence of oxygen in air.

(iii) Oxygen is essential for life. Without oxygen no living being could exist on earth.

(b) Carbondioxide

(i) A vessel containing a sample of clear lime water, when exposed to air, becomes covered with a white crust. When air is passed through lime water, it turns milky. Lime water absorbs carbondioxide from air to form insoluble calcium carbonate by the reaction,

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

Carbondioxide may be released from this calcium carbonate by dilute acids.

(ii) Plants absorb CO_2 from air in presence of moisture and sunlight with the help of chlorophyl in the green leaves. The process is known as photosynthesis.

(c) Moisture

(i) A sample of caustic soda exposed in air turns into liquid after some time due to absorption of water vapour present in air.

(ii) Fused calcium chloride also absorbs water vapour when exposed to air and turns into liquid.

(iii) Water vapour is responsible for the formation of clouds which condenses into rain.

(d) Nitrogen

After the chemical removal of water vapour and carbondioxide from air by passing it through soda lime which absorbs both CO_2 and H_2O, and then burning the air with phosphorus or passing it through heated copper which takes up oxygen, the residual gas contains mostly nitrogen. The residual colourless gas is non-inflammable. Nitrogen combines with heated magnesium to form magnesium nitride:

$$N_2 + 3Mg = Mg_3N_2$$

(e) Inert gases

These are left as ultimate residue after removal of all other constituents.

Liquid Air

Before air is liquefied, it is freed from moisture and carbondioxide because these gases are solidified easily on cooling and may clog the pipes of the liquid air machine. Dust, water vapour and carbondioxide are removed from the air successively through a dust catcher, fused calcium chloride and slaked lime. The purified air is then subjected to a pressure of about 200 atmospheres and cooled to remove the heat produced by compression. The cooling is generally done by means of a mixture of salt and ice, or by cold water in the jacket containing the pipe (Fig. 10—1).

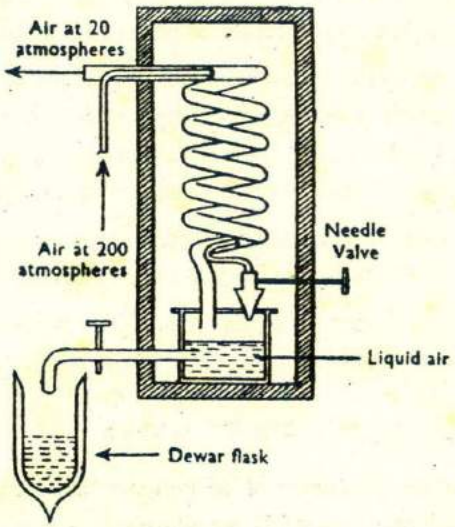


Fig. 10—1. A liquid air machine.

The cold compressed air is passed into the liquefying chamber through a needle valve where it expands suddenly to a pressure of about 20 atmospheres. This sudden expansion is accompanied by the absorption of heat and cools the air to a large extent due to Joule–Thomson effect. This cooled air is circulated round the spiral tube through the jacket, thereby further cooling the compressed air in the small inner coil of the liquefier. As the process continues, the air that escapes from the valve is colder than before, and finally the critical temperature is reached when the air becomes liquid.

Properties of liquid air

(i) Liquid air is a mobile liquid with a faint blue tinge.

(ii) Evaporates rapidly in the open with the absorption of a large quantity of heat. It is stored in Dewar flasks.

(iii) Liquid air is a mixture and, therefore, has no fixed boiling point. It boils at about −190°C (b.p. of oxygen, −182.5°C and nitrogen,−195.8°C).

(iv) Physical properties of many substances are changed in liquid air.

Applications of liquid air

(i) Manufacture of commercial oxygen, nitrogen and inert gases. Liquid oxygen is a fuel for rockets and jet-propelled planes and missiles.

(ii) Scientific researches at low temperatures. Thus, mercury freezes and becomes extremely hard in liquid air. Rubber, when immersed in liquid air, becomes hard and brittle. Fruits, flowers etc. become very hard. All metals become very good conductors of electricity when cooled in liquid air.

(iii) Chemical réactions at the temperature of liquid air are being carried out. Synthetic procedures of new compounds make use of cooling by liquid air.

(iv) Liquefaction of inert gases and subsequent separation by fractional distillation make use of liquid air.

THE INERT GASES

The elements of the zero group of the Periodic Table starting from helium, the second element (atomic number 2), are all gases. These are Helium (2), Neon (10), Argon (18), Krypton (36), Xenon (54) and Radon (86). All these gaseous

elements are generally known as inert gases since normally they do not react with other substances and exist only in the free state. The atoms of these gases do not even form diatomic molecules, but remain as separate atoms in the gaseous state. These are also called *Noble gases* because of their property of remaining aloof from other elements. These are also known as *Rare gases* because of their presence in the atmosphere in extremely minute amounts (total of about 1% only).

The Discovery of the Inert Gases

The discovery of inert gases is a thrilling episode in the history of chemistry. Until the end of the nineteenth century it was taken for granted that the atmosphere had been fully explored and none thought for a moment of searching for a new element in the air. In 1785, Cavendish had observed that when an electric spark was struck between two electrodes in an enclosed volume of mixture of oxygen and common air, the nitrogen of the air combined with oxygen which could be absorbed in alkali solutions. But a small volume of the air, about $\frac{1}{120}$th part, could not be converted to nitrous acid and remained as residue. This important experiment of Cavendish had also passed into oblivion.

About a century later, Rayleigh in 1892, performed experiments for accurate determinations of the densities of gases, such as nitrogen, oxygen etc. Although the oxygen which he prepared by three different methods from chemical compounds or isolated from air had the same density, the results with nitrogen were puzzling. The atmospheric nitrogen was found to be slightly heavier (to the extent of about 0.5%) than the nitrogen prepared by chemical methods, such as from ammonium nitrite, urea, oxides of nitrogen or nitric acid. The normal density of chemical nitrogen is 1.2505 *g./l* whereas the atmospheric nitrogen has a density of 1.2572 *g. /l.* Rayleigh repeated the experiment of Cavendish and confirmed the presence of unabsorbed residue.

It was known that each element gives its characteristic spectrum and from the spectral lines one can identify the elements. The spectrum analysis is a sort of finger print method for the identification of elements. Rayleigh was rather astonished to find that residual gas left after sparking nitrogen and oxygen did not give the spectrum of nitrogen but an unfamiliar type of spectrum.

Willium Ramsay gained permission from Rayleigh to investigate into the chemistry of the atmospheric air. He passed air over red hot copper in order to remove oxygen and the residual nitrogen was passed over heated magnesium to find out whether it would be completely absorbed or not. After the gas was passed back and forth over heated magnesium taking all precautions to exclude dust, water vapour and carbondioxide, everything was absorbed except about $\frac{1}{80}$th part of the original volume. The experiments of Ramsay on chemical nitrogen and atmospheric nitrogen are given schematically as follows :-

$$\text{Air} \xrightarrow[-CO_2]{-H_2O} N_2 + O_2 \xrightarrow[-O_2\,(CuO)]{\text{heated Cu}} N_2 \xrightarrow[-N_2(Mg_3N_2)]{\text{heated Mg}} \text{Residual gas}$$

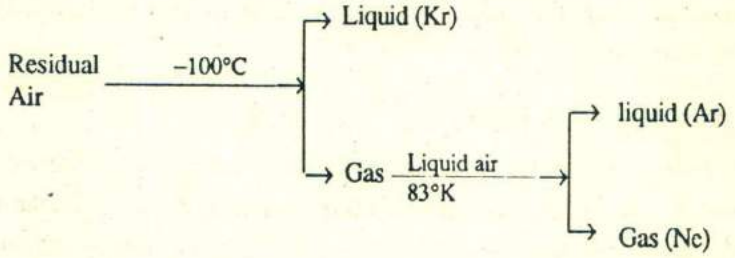
$$NO + Cu \rightarrow \underset{\uparrow}{\overset{NH_4NO_2}{\overset{\downarrow}{\text{Chemical}}}}\ N_2 \xrightarrow[-O_2]{\text{heated Cu}} N_2 \xrightarrow[-N_2]{\text{heated Mg}} \text{No residual gas at all}$$

$$NH_3 + Cl_2 \qquad \text{(if any)} \qquad (Mg_3N_2)$$

Rayleigh and Ramsay examined the spectrum of the residual gas and observed groups of green and red lines never observed before in the spectrum of any gas, A detailed study of this residual gas was made. The density of the purified residual gas was found to be 19.94 (H=1), its atomic weight was determined and chemical properties were investigated and was found to have no chemical activity. In 1894, Ramsay and Rayleigh announced the discovery of a new element, the first inert gas, and it was named Argon, "the lazy one", because of its chemical inactivity. Later on, it was proved that this residual gas was not pure argon but contained a number of other gases also.

In the year 1868, the French astronomer Janssen came to India to observe a total eclipse of the sun. He examined the chromosphere of the sun by means of a spectroscope and noticed a bright yellow line D_3, which did not coincide with D_1 and D_2 lines of sodium. Lockyer concluded that the new line did not belong to any element then known to exist in terrestrial substances. He named it Helium (helios for the sun) and for about two decades helium was regarded as hypothetical element which might possibly exist only in the sun.

In 1888, Hillebrand noticed that when the mineral uraninite or *cleveite* is heated with acid, an inert gas is evolved which he believed to be nitrogen and thus missed a great discovery. Ramsay repeated the experiments and obtained a sample of the gas by heating cleveite with dilute sulphuric acid. Nitrogen present in the gas was removed by the sparking method over caustic alkali. Ramsay identified the spectrum of this gas and confirmed the presence of helium in the minerals. Thus the terrestrial helium was discovered.



Ramsay and Travers observed that helium obtained from different minerals differed in density and by diffusion method separated the gases into two fractions differing in densities to a great extent. The heavier fraction gave the spectrum similar to that of argon and the lighter fraction was helium. Thus argon was also discovered in minerals.

After the discovery of argon and helium their positions in the Periodic Table presented a problem. It was suggested that helium with atomic weight 4 might possibly belong to a new group of elements. The possibility of the existence of one element between helium and argon and at least two or more of higher atomic weights were suggested. Since argon was discovered in the residual gas obtained after removing the oxygen and nitrogen, Ramsay and Travers suspected the presence of other gases of similar nature in the residual gas. Starting with liquid air, by fractional evaporation and spectral analysis of the fractions, they first discovered a new inert gas in 1898 which was named Krypton (meaning hidden). After working on the density of this gas, it was found that the new element belonged between bromine and rubidium.

Continuing their search for the lighter gas, the residual air or mainly argon in the liquid state was subjected to fractional distillation under reduced pressure.

The more volatile fraction gave a complex spectrum with many brilliant red lines. The blaze of crimson light brought honour and fame to Ramsay and Travers. The new gas was named Neon (the new one) in 1898.

Ramsay and Soddy, in 1903, made the sensational discovery that helium was also produced by the atomic disintegration of radium. Later on, it was shown that many radio-elements on disintegration produce helium.

Dorn, in 1900, discovered radium emanation (Radon) as one of the disintegration products of radium. Radon resembled all other inert gases in the chemical inactivity.

Sources of the Inert Gases

(1) Inert gases in the air : The inert gases are present in the air to a total of about 1%. Apart from argon, all other inert gases are present in the air in very minute amount and hence the name *rare gases*. The compositions of the inert gases in the air are :

Argon	0.932%
Neon	0.0015%
Helium	0.0005%
Krypton	0.0001%
Xenon	0.00001%

(2) Other sources of inert gases : Some minerals, such as uraninite, monazite, thorianite, cleveite etc. contain helium and also some argon which are evolved when the minerals are heated.

(3) The most important source of helium is the natural gas (mainly methane) from some petroleum springs.

(4) Inert gases are also present in some hot springs having their sources at great depths.

Isolation of Inert Gases

Helium: 1. Helium may be isolated from various sources and purified. The most important source of helium is the natural gas from petroleum springs in the U.S.A. and Canada. Helium is obtained from the natural gas by cooling to a

very low temperature whereby all other gases present become solid or liquid and helium is left in the gaseous state.

2. Helium may be obtained from monazite by strong heating or by heating the mineral with dilute sulphuric acid. Helium thus obtained contains mainly other gases as impurity.

3. From hot springs helium may be collected by simple devices. This helium contains mainly argon as impurity.

Purification of helium is easily done by contact with coconut charcoal which, at the temperature of liquid air, absorbs all other gases except helium, hydrogen and neon. The coconut charcoal method is also applied to isolate the inert gases from one another and prepare samples of the gases.

Isolation of the Mixed Inert Gases

The mixed gases are allowed to come in contact with coconut charcoal in a bulk kept immersed in a cold bath in Dewar flask.

After about half an hour the unabsorbed gases are pumped off (Fig. 10—2).

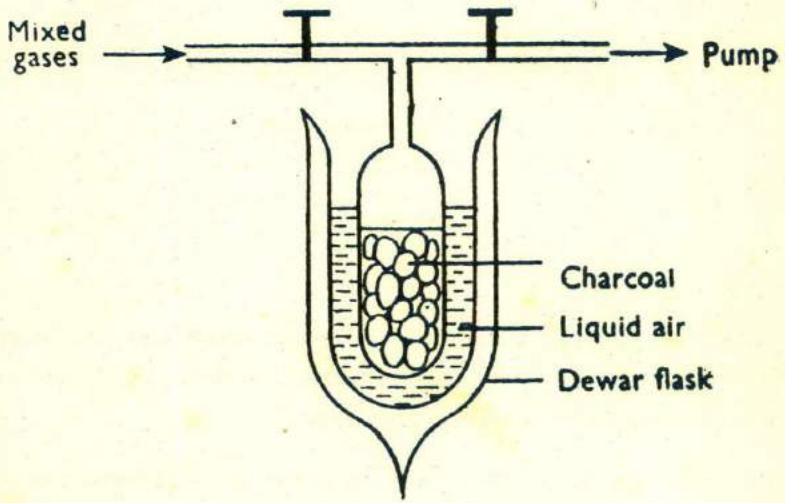
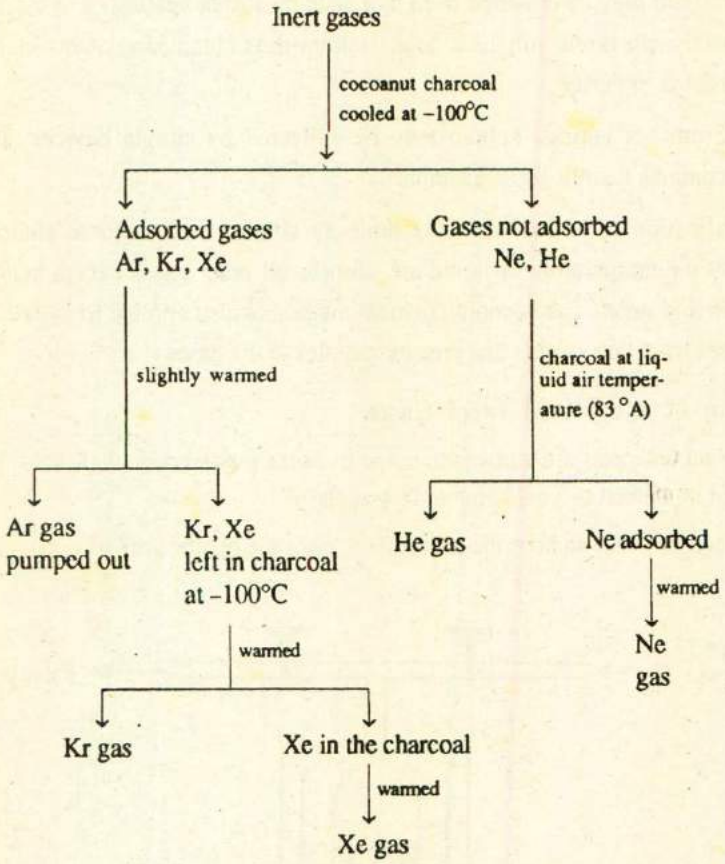


Fig. 10-2. Purification of inert gases (He) by coconut charcoal.

The plan of isolation of inert gases by this method is as follows :-



Argon : Argon is generally obtained from air which is the chief source. The isolation of the atmospheric argon is carried out in large scale. There are several procedures for the isolation of argon from air.

1. Ramsay's original method : Air freed from dust, carbondioxide and water vapour, is passed through a tube containing heated copper which removes oxygen (as CuO) and the issuing gas is then passed through heated magnesium

which removes nitrogen (as Mg_3N_2). The residual gas contains mainly argon and other inert gases and is purified.

2. Rayleigh's method : A mixture of 11 volumes of oxygen and 9 volumes of air is subjected to electric discharge from a transformer of 6000-8000 volts, thereby nitrogen and oxygen of air combine to form nitric oxide. A fountain of caustic soda solution is discharged through a tube in the inside of the vessel to dissolve the nitric oxide formed. Impure argon was obtained by removing excess oxygen by means of alkaline pyrogallol solution.

3. Calcium carbide process : A mixture of 90 parts calcium carbide and 10 parts calcium chloride is taken in an iron retort and heated to redness (800°C). Air is passed through the heated mixture. The issuing gas is passed over red hot copper oxide (CuO) to convert CO to CO_2 and then through solid KOH to absorb CO_2 and moisture. Final traces of moisture is removed by means of P_2O_5. The gas, rich in argon, is stored in gas holders. The reactions that occur, remove oxygen and nitrogen as follows :

$$CaC_2 + N_2 = CaCN_2 + C$$

$$2C + O_2 = 2\,CO$$

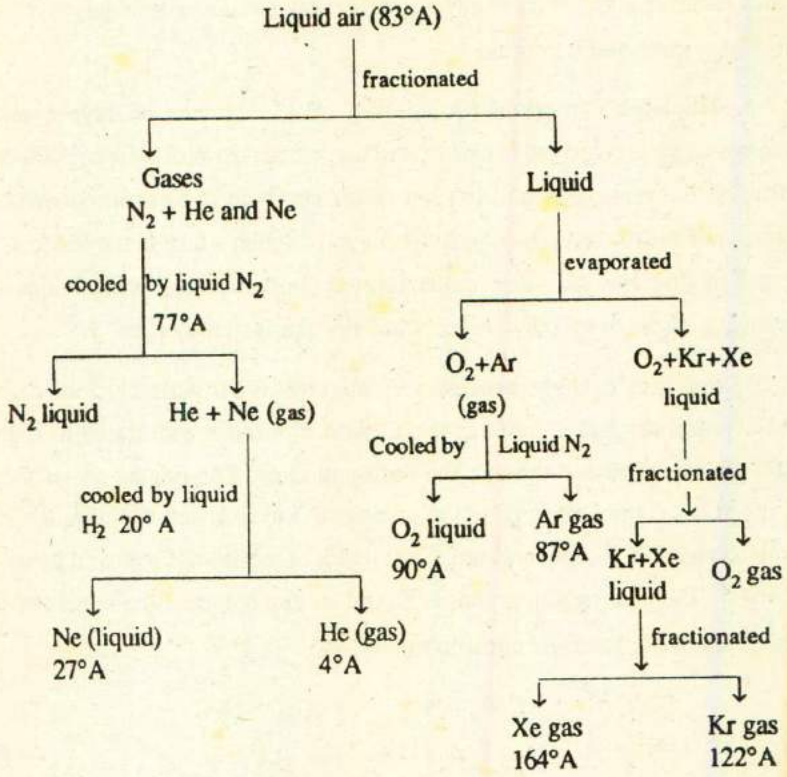
$$2C + 2O_2 = 2\,CO_2$$

$$3CO_2 + 2CaC_2 = 2\,CaCO_3 + 5C$$

CO formed during the reaction is removed by CuO :

$$CuO + CO = Cu + CO_2$$

Argon and other inert gases : These are also obtained from liquid air by fractional liquefaction and evaporation at reduced pressure. There are quite a great deal of differences in the boiling points of the various constituents of liquid air. The plan of separation of all the inert gases may be outlined as follows and industrially used for the separation of all the inert gases.



Radon : Radon resembles in all other properties to the family of inert gases. It differs only in its radioactivity and undergoes spontaneous disintegration.

Radon is continually formed by the radioactive change of radium metal and its compounds under all conditions by the loss of He atoms or α-particles. The equation for the change is,

$$_{88}Ra^{226} = {}_{86}Rn^{222} + {}_{2}He^{4}$$

Radon is best produced from an aqueous solution of a radium salt. Radium salt is dissolved in water and the solution is allowed to stand. On boiling the solution, radon is evolved along with some helium, oxygen and hydrogen.

The Monoatomic Character of the Inert Gases

(1) The weights of 22.414 litres of the inert gases at N.T.P. have been found to be :

He	4.003 g.
Ne	20.183 g.
Ar	39.94 g.
Kr	83.80 g.
Xe	131.30 g.
Rn	222.00 g.

The above figures, therefore, give the molecular weights of the different inert gases. But these are also their respective atomic weights. It has already been stated that ordinarily the inert gases are devoid of chemical activity.

(2) The monoatomic nature was also proved by the measurement of specific heats of the gases. A gas molecule if it is diatomic or more complex molecule, by virtue of its three forms of motion, i.e., translational, vibrational and rotational, would require greater amount of energy to raise its temperature by 1°C than a molecule which is capable of only one kind of motion, e.g., translational motion. The inert gases have lower specific heats than hydrogen or oxygen and it is concluded that they occur as individual atoms. It has been shown that all the gases in which the ratio between the specific heat at constant pressure, C_p, and specific heat at constant volume, C_v, (C_p/C_v) is equal to about 1.667, are monoatomic. The ratio for diatomic gases is about 1.4 and for triatomic gases 1.3. Experimental determinations of C_p/C_v of all the inert gases have given values ranging from 1.64 to 1.68. Hence the inert gases are monoatomic.

The electronic structures of the inert gases indicate that all the gases have electronic structures which are paired and have completely filled s or s and p orbitals as given in Table 10.2.

Table 10.2. Electronic structure of the inert gases.

At. No.	*Elements*	*Electronic configurations*
2	He	$1s^2$
10	Ne	$1s^2 2s^2 2p^6$
18	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$
36	Kr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
54	Xe	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2\ 4p^6 4d^{10} 5s^2 5p^6$
86	Rn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$

Thus it may be concluded that an electronic structure represents an stable system in which all the electrons are paired and s and p orbitals in the outermost energy levels are completely filled. The elements possessing such electron arrangements must have a very stable atom and hence devoid of chemical activity. This fact is proved by the ionization potential of the inert gases as shown in Fig. 3—1.

Properties of the Inert Gases

1. Physical Properties

All the inert gases are colourless, odourless and tasteless. They are somewhat soluble in water. Helium is the least soluble of all gases. All the gases can be liquefied and helium is the most difficult to liquefy. Liquid helium has been obtained first by Onnes in 1907 by the Joule-Thomson effect on the gas cooled previously to 15°A. The colourless liquid has very low density and has the lowest boiling point of all liquids, 4°A. Solid helium has been obtained by cooling liquid helium to 1°A under pressure. Liquid helium exists in two forms: He-I and He-II having a transition point but no triple point. Metals in liquid helium become superconductors of electricity. Liquid He-II has lowest viscosity and can flow upward along the surface of a glass container.

Radon gas glows strongly emitting heat and energy. Liquid and solid radon are colourless but glow with a bluish tinge in the dark.

The physical properties of the inert gases are summarized in Table 10.3.

Table 10.3. Physical properties of the inert gases.

Properties	*He*	*Ne*	*Ar*	*Kr*	*Xe*	*Rn*
1. Atomic Number	2	10	18	36	54	86
2. Electrons in the outermost levels	s^2	s^2p^6	s^2p^6	s^2p^6	s^2p^6	s^2p^6
3. Atomic wt.	4.0	20.2	40	83.8	131	222
4. Atomic radius Å	0.93	1.60	1.91	2.0	2.2	—
5. Melting point °C	−272	−249	−187	−157	−112	−71
6. Boiling point °C	−269	−246	−186	−153	−107	−62
7. Critical temp. °C	−286	−220	−117	−63	−15	−104
8. Critical pressure (atmospheres)	2.26	26.9	48.0	54.3	58.2	62.4
9. C_p/C_v	1.65	1.64	1.65	1.69	1.67	—
10. Colour of spectra	Yellow	Red	Orange	Green	Blue	—

A comparison of the boiling points of the inert gases with other substances of comparable molecular weights is given in Table 10.4 to show the extremely low values for the inert gases.

Table 10.4. Comparison of the boiling points (b.p.) and molecular weights (M.W.) of the inert gases with other comparable substances.

Substances	*M. W.*	*b. p. (K)*
He	4	4.2
H_2	2	20.3
Ne	20	27
CH_4	16	92
Ar	40	87
HCl	37	189
Kr	84	121
CF_4	88	135
Xe	131	164
$n\text{-}C_9H_{20}$	128	424
Rn	222	211
ICl_3	233	350

II. Chemical Properties

The electronic configuration and the nature of the inert gases: The chemical activity and the valence of an element depends upon the electronic configuration, particularly upon the type, the number and the arrangement of the electrons in the outermost energy level. The number of electrons in the outermost level of the inert gases is 8 derived from s^2p^6 arrangement. In the case of helium it is 2 having $1s^2$ electrons. Since these arrangements represent completed electronic level and account for chemical inactivity because of no tendency to alter the electronic arrangements by transfer or sharing of electrons, therefore, the inert gases do not even combine among themselves to form molecules but exist in monoatomic conditions.

The atoms of the inert gases have no electron affinity and do not gain electrons from reducing agents. They have higher ionization potential than those of any other elements and thus do not tend to lose electrons to oxidizing agents. On the other hand, many ions assume the stable electronic arrangement of the inert gases.

Compound of the Inert Gases

In spite of the inert character of the inert gases, attempts have always been made to force them to enter into chemical combination by using unusual conditions with success. The tendency of compound formation by inert gases increases as the atomic number increases. Inert gas with higher atomic number have **d** orbitals available which participate in bond formation. He, Ne and Ar show less tendency to form compounds in view of low bond energies of their compounds. Xe, by far, gives large number of compounds while Rn chemistry is rather complicated because of its radioactive nature.

(1) Boothe and Wilson on the basis of thermal analysis showed the existence of a series of argon-boron trifluoride compounds at low temperatures :

$Ar : BF_3$, $Ar : 2BF_3$, $Ar : 3BF_3$ and so on.

These compounds have similar bonds as in the following molecules :

$NH_3 : BF_3$ and $(CH_3)_2O : BF_3$

(2) The dipole interaction of H_2O molecule may polarize an inert gas and hydrate formation has been claimed having the following formula and exists at low temperatures and high pressures :

$Ar : xH_2O$ $Kr : xH_2O$ $Xe : xH_2O$ where x is 1 to 6.

(3) Helides (from helium) of some metals have been made, such as HgHe, $HgHe_2$, WHe_2, FeHe etc. These "compounds"may be alloys in which small helium atoms occupy the interstitial positions in the crystal lattice and may not be true chemical compound.

(4) The inert gases become incorporated into the crystals of hydroquinone the molecule of which acts like a *cage*. These types of compounds are known as *clathrates* or cage compounds. They break up when the crystals are melted or dissolved in water; thereby the free gas is released.

(5) More recently xenon has been shown to form definite compounds particularly with the most electronegative element fluorine. XeF_4 has been isolated in pure crystalline form. Other fluorides such as XeF_2 and XeF_6, have also been made. Oxygen is also shown to form compounds with xenon. XeO_3, $XeOF_4$ and XeO_2F_2 have been isolated from the reaction products of xenon fluoride and water : $XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$ and

$$XeOF_4 + 2H_2O \rightarrow XeO_3 + 4HF.$$

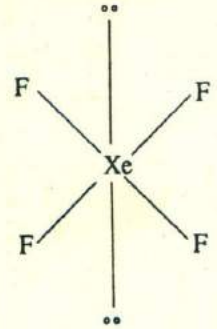


Fig. 10—3. Structure of XeF_4.

The structure of stable XeF_4 molecule has been found to be square planar with Xe—F bond = 1.93 Å. Since there are four pairs of electrons (8 electrons) in the outermost energy level of Xe, the formation of XeF_4 crystals can be explained on the basis of octahedral arrangement using sp^3d^2 hybridized orbitals of Xe having two axial positions occupied by two electron pairs as given in Fig. 10–3.

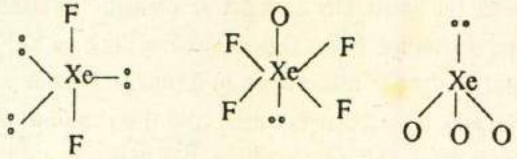
The formation of Xe—F bonds in XeF_4 may be shown as follows on the basis of electron arrangements :—

Xe—$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$

Xe—Outermost energy level—$5s^2\ 5p^6$

	$5s^2$	$5p^6$			$5d^0$				
Xe (ground state)—	↿⇂	↿⇂	↿⇂	↿⇂	—	—	—	—	—
Xe (excited states)—	↿⇂	↿⇂	1	1	1	1	—	—	—
XeF_4—	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂			
			F	F	F	F			
			sp^3d^2						

Other compounds of Xe are formulated as follows :



(XeF_2) $(XeOF_4)$ (XeO_3)

sp^3d sp^3d^2 p^3d

Uses of the Inert Gases

1. Uses of Helium :

(a) Because of its lightness and non-inflammability, helium is used for filling observation balloons.

(b) Helium is less soluble than nitrogen in the blood. Hence mixture of helium and oxygen are used by sea divers. This overcomes the disadvantage of using air at high pressure for respiration, because the nitrogen of air gets dissolved in the blood at high pressure and on surfacing the pressure is released but the dissolved nitrogen forms a pathological condition known as *bends* due to the formation of bubbles of nitrogen in the blood giving sudden pain.

(c) Mixtures of helium and oxygen are also used in the treatment of respiratory diseases such as asthma.

(d) Helium is used for inflating tyres of large aeroplanes.

(e) It is also used as an inert atmosphere for the melting and welding of easily oxidizable metals.

(j) Liquid helium produces lowest temperature and is used for scientific research.

(g) It is used in tube lights, vacuum drying etc.

2. Uses of Neon :

(a) Neon is used in neon lamps and signs. When an electric current is passed through neon under low pressure, it emits a brilliant orange-red glow which penetrates through mists and fogs. This is, therefore, used as beacon lights for air pilots.

(b) Neon is now-a-days extensively used in advertisement signs by coloured lights and in fluorescent tubes. The colour of neon in a lamp or tube may be changed by mixing with argon and mercury vapour and by using tubes made of glasses of special compositions. Lights of different shades can thus be obtained.

(c) Neon is used in television sets, radio-photography, sound movies etc. where ready responses to changes in electrical potential are required.

(d) Neon is also used for stimulation of growth of plants and flowers in the green houses.

3. Uses of Argon :

(a) Argon is used in gas-filed electric bulbs. It lowers the heat conductivity and complete chemical inertness makes it preferable to nitrogen. Thus the volatilization of tungsten filament is reduced and prolongs the life of the lamp. Ordinary tube lights contain a mixture of argon and mercury vapour

(b) With oxygen argon is used in welding to create an inert atmosphere. Argon is now widely used for welding of aluminium and stainless steel.

(c) Geiger-Counters are also filled with argon.

4. Uses of Krypton and Xenon :

(a) Krypton-xenon photographic flash tube has been developed for taking high speed photographic exposures. In cinematography, krypton flash is used to produce intense light.

(b) Krypton mixed with neon gives blue light in the electric tubes.

(c) Xenon imparts green colour to the electronic tube lights.

(d) Krypton is used in ionization chambers for cosmic ray measurements.

(e) Xenon has recently been used for making Bubble Chambers for detecting γ-rays, neutrons and other nuclear particles.

5. Uses of Radon :

Radon differs from other inert gases in its radioative properties. Because of this property radon is used in the radiotherapy of malignant growth. It is particularly suitable in the non-surgical treatment of cancer. Radon is much more radioactive than radium and the therapeutic preparation of radon in small tubes is technically known as *seeds*.

QUESTIONS AND PROBLEMS

1. How were helium. neon, and argon discovered.? What are the properties and uses of these gases ?
2. (a) Name the inert gases. Explain why they are inert and discuss their position in the Periodic Table of elements.
   (b) What are the important applications of the inert gases?
3. (a) Give a short account of the discovery of inert gases of the atmosphere. Why are these so called?
   (b) Discuss the important properties of the inert gases and mention some of their uses.
4. (a) What are inert gases? Show that the Bond Orders in He_2 and Ne_2 are zero.
   (b) Write a short account of the discovery of inert gases.
   (c) Explain why inert gases are chemically inactive.
   (d) Mention four uses of inert gases.
5. Give a short historical accounts of the discovery of Argon and Helium. How can they be separated and to what industrial use they have been put? Discuss the position of inert gases in the Periodic Table.
6. Describe the methods employed indicating the physico-chemical principle involved in the separation of rare gases of the atmosphere. Indicate their importance in chemistry.
7. What physical principles are employed in the liquefaction of air? What are the uses of liquid air?
8. Relate the chemical inactivity of the inert gases to their electronic structure.
9. How is argon obtained in a pure state? State its uses.
10. Give a brief account of the discovery of inert gases, their properties and uses.
11. Discuss the important properties of the inert gases and mention some of their uses.
12. Write notes on :- Discovery of inert gases and its impact on periodic classification.
13. Discuss "Elements of zero group are highly inert".
14. Why the tendency for compound formation of inert gases increases as the atomic number of elements increases ?
15. Write equation for the reaction of XeF_4 with H_2O.
16. Explain why $XeBr_2$ has not been prepared.
17. Compare the structure of ICl_2^- and $XeCl_2$.
18. $O_2^+PtF_6^-$ isolated by Bartlett gave rise to the preparation of $Xe^+PtF_6^-$. Compare the ionization energies of O_2 (278.5 Kcal/mole) and of Xe (279.7 Kcal/mole) and the oxidation potential of O_2 (g) and Xe(g) are 12·2 ev and 12'12 ev respectively to justify the reason of formation of the inert gas compounds.

CHAPTER 11

HYDROGEN, WATER & HYDROGEN PEROXIDE

HYDROGEN

Hydrogen is the first element of the Periodic Table. By and large, hydrogen forms more compounds than any other element in the Periodic Table; much more than even carbon in organic chemistry.

Sources of Hydrogen

1. Hydrogen is the most abundant element in the universe. It is believed that 90% of the weight of the sun consists of hydrogen, so also other stars. This information is gathered by examining the solar spectra and spectra of stars.

2. Water is the most abundant compound of hydrogen on the earth.

3. All organic compounds and natural organic substances contain hydrogen.

4. Hydrogen rarely occurs in the free state on the earth.

Preparation : Hydrogen is prepared both for experiment in the laboratory and on a large scale for industrial uses.

1. In the laboratory it is made by the action of an acid on zinc or other metals lying between magnesium and tin in the Activity Series of metals. The reaction takes place with the hydrogen ion H_3O^+ :

$$2H_3O^+ + Zn \longrightarrow Zn^{+2} + H_2 + 2H_2O$$

Notice that this is an oxidation-reduction reaction.

2. Metal hydrides react with water to produce hydrogen, Thus,

$$LiH + H_2O \longrightarrow LiOH + H_2$$

$$CaH_2 + H_2O \longrightarrow Ca(OH)_2 + H_2$$

3. Commercially hydrogen is produced by passing steam over red-hot iron :

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

4. The least expensive method for producing commercial hydrogen is the water gas process in which steam is passed over hot carbon :

$$C + H_2O \rightleftharpoons CO + H_2$$

Notice that mixture of CO and H_2 are formed and generally the two gases are not separated. The mixture of CO and H_2 is known as water-gas and makes an excellent fuel. The mixture may be separated by fractional liquefaction.

5. The purest form of hydrogen is obtained by electrolysis of water :

$$2H_2O \rightleftharpoons 2H_2 + O_2 - 135 \text{ Kcal}$$

The oxygen is evolved at the anode and hydrogen at the cathode. The decomposition reaction is endothermic and requires supply of energy in the form of electric current. In practice alkaline solutions are electrolysed although acidulated water can also be used.

6. Mixture of CO + H_2 is also obtained when CH_4 from natural gas and steam is passed over heated catalyst (Cu or Ni) under pressure:

$$CH_4 + H_2O \xrightarrow[\text{catalyst}]{\text{Ni}} CO + CO_2 + H_2$$

$$2CO + O_2 \longrightarrow 2CO_2$$

Hydrogen is combined with nitrogen to form ammonia which reacts with CO_2 to products urea.

$$N_2 + H_2 \xrightarrow[\text{catalyst}]{\text{Fe}} NH_3$$

$$2NH_3 + CO_2 \xrightarrow[\text{atm.}]{\text{31°C, 200—300}} NH_2CONH_2 + H_2O$$

Properties of Hydrogen

Physical Properties : Hydrogen is the lightest of all known substances. It is a colourless, odourless gas slightly soluble in water. It is combustible. The following figures of the physical constants in Table 11.1 indicate some of the physical properties.

Table 11.1. Properties of hydrogen.

Atomic number	1
Atomic wt.	1.008
Bond energy in H_2	103 Kcal/mol.
Bond length in H_2	0.75Å
Melting point	14° Absolute (K)
Boiling point	20° Absolute (K)
Critical temperature	33° Absolute (K)
Inversion temperature	195° Absolute (K)
Density at N. T. P.	0.09 g/l (STP)

Hydrogen has very low m. p. and b. p. indicating small intermolecular attraction in geseous hydrogen molecule. Inversion temperature of 195°A indicates that when hydrogen gas is cooled to below 195°A, release of pressure produces cooling and liquefaction. Above 195°A, release of pressure produces warming. Hydrogen diffuses faster than any other gas because of the lowest molecular mass than all gases.

Electronic Structure : Hydrogen has only one electron, $1s^1$. All the alkali metals have also s^1 electrons in the valence shell, but after the stable groupings of s^2p^6 electrons. But the hydrogen electron is directly outside the nucleus which has no neutron but only proton. This difference in the electron position makes the chemistry of hydrogen different from that of alkali metals. The absence of inner completed electronic shell leads to certain differences in the properties of H and He with outer elements having similar configurations of the outer electrons.

Because the nucleus of the hydrogen atom consists of proton, a fundamental particle, it is of great importance in the field of nuclear chemistry and the cosmic chemistry of the universe.

Hydrogen molecule is diatomic, H_2. During chemical reaction the molecule H_2 reacts by breaking the H—H bond for which quite high energy is required and H_2 reactions are generally slow.

Chemical properties : As mentioned, the chemical properties of hydrogen require the breaking up of the bond in H_2 molecule. This is quite readily achieved at elevated temperature. H_2 though relatively inactive at ordinary

temperature, enters into chemical combinations in a variety of ways mostly at elevated temperature :

(1) Hydrogen enters into chemical reaction by losing its electron, the compounds formed contain hydrogen in the +1 oxidation state.

(2) Hydrogen enters into chemical combination with other elements by gaining electron, the compounds formed have hydrogen in the –1 oxidation state.

(3) Hydrogen also combines with some metals with 0 oxidation state.

HYDRIDES

Binary compounds of hydrogen with another element is generally known as *hydrides*. Depending upon the mode of combination three types of hydrides are generally formed : (a) covalent or molecular hydrides (usually volatile). (b) ionic or salt-like hydrides, (c) metallic or interstitial hydrides.

1. Compounds containing hydrogen in +1 oxidation state : This is the most common combination of hydrogen and this happens when hydrogen combines with more electronegative elements than itself. Thus F, O, N, C etc. form HF, H_2O, NH_3, CH_4 respectively containing hydrogen in the +1 oxidation states.

Thus hydrogen combines with non-metals directly under suitable conditions. With F_2 it combines at very low temperature to form HF :

$$H_2 + F_2 = 2HF$$

Hydrogen combines with oxygen when ignited with release of energy.

$$2H_2 + O_2 = 2H_2O$$

With nitrogen it combines under pressure and in presence of a suitable catalyst to form NH_3 :

$$3H_2 + N_2 = 2NH_3$$

It may be noted that in all such compounds the hydrogen is not actually present as H^{+1} but the bonding is mostly covalent with some degrees of ionic character depending upon the difference in electronegativity of the other elements and hydrogen. In acids and acid salts the +1 oxidation state of hydrogen is more pronounced as in $NaHSO_4$, NaH_2PO_4 etc.

2. Compounds containing hydrogen in –1 oxidation state : These are compounds in which hydrogen has gained an electron to form hydrogen H^- ion. When hydrogen combines with elements such as Li, Na, Ca etc. which are less electronegative than itself, the compound formed contains hydrogen in the –1 oxidation state. These compounds actually contain the true hydride ion (H^-) and a positive metal ion and behave like ionic compounds or salts. Therefore, they are also called salt-like hydrides.

When the alkali metals are heated in hydrogen gas, alkali metal hydrides are formed. These are white crystalline solids :

$$2Na + H_2 = 2NaH$$

Similarly, alkaline earth metals form the hydrides such as CaH_2, BaH_2 etc.

Some metal hydrides are regarded as salt-like, but are not ionic and are prepared by special methods rather than by direct union of the elements with hydrogen. Some of these are CuH_2, MgH_2, AlH_3, HgH_2 etc. although these appear to contain H^- ions but are less stable.

Salt-like hydrides of alkali metals conduct electricity in the molten condition and on electrolysis hydrogen gas is evolved at the anode proving H to be present as H^- state.

The hydride ions (H^-) are unstable in water and are oxidized to H_2:

$$LiH + H_2O = H_2 + LiOH$$

Complex hydrides are lithium aluminium hydride, $LiAlH_4$, sodium borohydride, $NaBH_4$ etc. In these cationic and anionic species are :

$$Li^+ \ AlH_4^- \qquad\qquad Na^+ \ BH_4^-$$

These complex hydrides are solids and react with water to give H_2. They are conveniently used as reducing agents in organic chemistry.

3. Compounds containing hydrogen in the 0 oxidation state : These compounds are generally known as metallic or interstitial hydrides. Thus uranium, palladium, zirconium etc. form hydrides by direct combination with hydrogen. These hydrides have metallic properties and do not form compounds of

fixed composition except in uranium hydride having the formula UH_3. The compound with palladium may be represented as PdH_n.

It is believed that these hydrides contain proton with a single electron (H atom) in the interstices of the metallic structure. Hydrogen is dissolved as elementary hydrogen in the metals and hence it is present in the 0 oxidation state.

Reaction of hydrogen with compounds

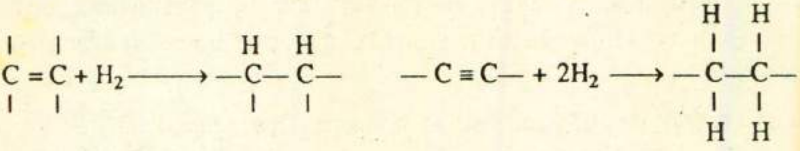
(1) Heated oxides of less electropositive and transition metals react with hydrogen with the formation of metal and water :

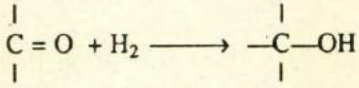
$$CuO + H_2 = Cu + H_2O$$

Sometimes a lower oxide of metal is also formed :

$$MnO_2 + H_2 = MnO + H_2O$$

(2) In presence of catalysts and at elevated temperature the following reactions take place :





Thus $CO + 2H_2 \xrightarrow{\text{catalyst}} CH_3OH$

Such reactions are known as hydrogenation in which hydrogen is added to the molecule. These reactions are of great industrial importance.

Uses of Hydrogen : (1) Hydrogenation of materials such as of N_2 (for NH_3), CO (for CH_3OH), coal, organic products and vegetable oils (for margarine) etc. are the most important fields of its application. (2) in oxyhydrogen and atomic hydrogen flames for welding. (3) As water gas in fuel. (4) Hydrogen bomb.

Atomic Hydrogen : When H_2 gas is passed through an electric arc of tungsten wire at low pressure, it dissociates into atoms giving atomic hydrogen. The atomic hydrogen is very reactive and combines with non-metal such as S, P, As to form hydrides. With O_2 it gives H_2O_2. When the atomic hydrogen is blown out of the tungsten arc by hydrogen gas, an intense heat is generated due to the combination of atomic H to form H_2 (heat of formation of H_2). The atomic hydrogen torch is used in welding.

Nascent Hydrogen : It has been presumed that at the instant when hydrogen is produced by means of chemical reactions, it is in the atomic state which ultimately combines in the molecular form and is evolved as H_2. Thus Sn and HCl or Zn and H_2SO_4 produce nascent hydrogen at the instant when they react and have reducing properties and reduce Fe^{+3}, Cr^{+6} to Fe^{+2} and Cr^{+2} state respectively.

Hydrogen Bond : One of the most important properties of hydrogen is its ability to form Hydrogen Bond. When hydrogen forms a bridge between two electronegative atoms of adjoining molecules, it is said to form a hydrogen bond. (see Chapter 2 page 100)

Ortho and Para Hydrogen

As the electron is considered to be spinning on its own axis, similarly, the nucleus (protons and neutrons) have spins. Hydrogen molecule consists of two protons and these are spinning on their own axes. The conditions arise when two protons combine to form the hydrogen molecule. The two protons may be spinning in the same direction (parallel spins) or the two may be spinning in opposite directions (antiparallel). Hydrogen molecules containing parallel nuclear spins are known as ortho hydrogen and those having nuclear spins in opposite directions are called para hydrogen as shown in Fig. 11—1.

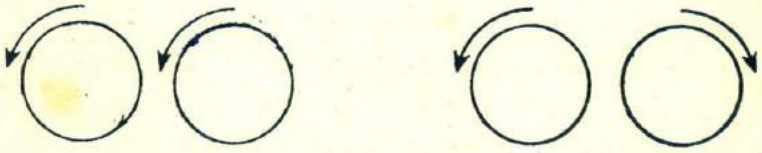


Fig. 11—1. Ortho and para hydrogen.

Ortho and para hydrogen have somewhat different physical properties and their stabilities differ at different temperatures. Information about such molecular rotation is often obtained by the study of molecular spectra. At room temperature 75% of ortho hydrogen is present in the ordinary hydrogen. At low temperature, proportion of para hydrogen increases.

Isotopes of Hydrogen

Hydrogen occurs in nature in the form of three isotopes. They are,

$_1H^1$ Hydrogen, protium, p;

$_1H^2$ Deuterium, heavy hydrogen, deutron (Deuterium), D;

$_1H^3$ Tritium, T.

There is only a very tiny amount of tritium in hydrogen. One atom of tritium is present for every 10^7 atoms of hydrogen; similarly, one atom of deuterium for 5×10^3 atoms of hydrogen. There is quite considerable difference in the masses of the hydrogen atoms and this gives rise to quite appreciable difference in physical properties and also in chemical properties. The differences in properties arising out of the masses of isotopes are called *Isotopic Effect*. Thus the isotopic effect is maximum in the case of hydrogen isotopes than any other elements. Deuterium and tritium, because of their greater masses, have lower vapour pressures than ordinary hydrogen. These heavier isotopes become concentrated in the last portion of liquid hydrogen when it is allowed to evaporate.

Deuterium is of great importance in connection with heavy water and tritium in nuclear fusion reaction for creating hydrogen bomb.

WATER

There is no other chemical substance which is so much familiar to us as water. Nearly three-fourths of the earth's surface is covered with water. The air and vegetable world contain high percentages of water. Water is a chemical of unique properties and hence its manifold applications.

Physical Properties of Water

Water, when pure, has no colour, no taste and no odour. The pleasant taste of water is due to dissolved gases and salts. Some physical constants are given in Table 11.2.

Table 11.2 Physical properties of water.

Melting point	0.0°C
Boiling point at 760 mm.	100.0°C
Density at 4°C	1.0 g/ml.
Heat of fusion	79.7 cal/g.
Heat of vaporization	539.6 cal/g.

The amount of heat required to change the state of water or to raise its temperature is quite large as compared to other substances. Again, an interesting property is its highest density at 4°C. Similarly, the expansion in volume on freezing makes solid water (ice) float on the surface.

Purification of Water

All natural waters are impure because of dissolved and suspended impurities. Sea water contains about 4% of dissolved solids. The following impurities may be present in water and their presence and quantities may vary according to the sources :—

1. *Suspended impurities :* Fine sand, clay, organic micro-organisms etc.

2. *Dissolved impurities :* Gases such as carbondioxide, oxides of nitrogen, nitrogen, oxygen, argon, helium etc. Solids such as chlorides, sulphates and bicarbonates of Na, Mg, Ca, Al, Fe, potassium etc.

Purification of water is necessary both for human consumption and industrial applications. The great demand of pure water for city uses and for industries has created a world-wide problem.

Hard Water : Water containing soluble calcium, magnesium salts are known as *hard water*. These are generally the sulphate, chloride and bicarbonate of calcium and magnesium. When only the bicarbonates of calcium and magnesium are present in water, the hardness is called *temporary*. But when the sulphate and chloride of calcium are present, the hardness is known as *permanent*. Hard water reacts with soap and gives rise to the precipitates of

insoluble calcium stearate. In boilers hard water forms insoluble crusts known as *boiler's scale* due to precipitation of insoluble carbonates etc. on the inside surface of the boilers and also tubes. This scale is a poor conductor of heat and causes waste of energy.

Hence removal of hardness of water is essential both for washing and industrial purposes.

Softening of Water : The process of removing hardness is called softening of water.

(1) ***Boiling*** : Temporary hardness can be removed by boiling, in which case the bicarbonates of calcium or magnesium are decomposed :

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + CO_2 + H_2O$$

(2) ***Liming*** : Temporary hardness can also be removed by adding lime or an aqueous solution of ammonia :

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 + Mg(OH)_2 + 2H_2O$$

$$Ca(HCO_3)_2 + 2NH_3 \longrightarrow CaCO_3 + 2NH_4^+ + CO_3^{-2}$$

(3) ***Caustic Process*** : Non-carbonate hardness or permanent hardness is removed by adding Na_2CO_3 or crude NaOH :

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$

$$MgSO_4 + 2NaOH \longrightarrow Mg(OH)_2 + Na_2SO_4$$

(4) ***Calgon Process*** : Sodium hexametaphosphate, $(NaPO_3)_6$, commercially known as *calgon*, is also used for softening. It reacts with Ca^{+2} and Mg^{+2} to form a soluble complex ion :

$$2Ca^{+2} + Na_2[Na_4P_6O_{18}] \rightleftharpoons 6Na^+ + [Ca_2P_6O_{18}]^{-2}$$

(5) ***Permutit Process*** : Complex sodium-alumino-silicate, which is known as permutit or synthetic *zeolite*, is used for water softening by a process called *Ion-exchange*. Water containing Ca^{+2} and Mg^{+2} ions are exchanged with harmless Na^+ ion in the permutit bed. The permutit bed can be regenerated for use by means of strong NaCl solutions :

$$2NaAlSi_2O_6 + Ca^{+2} \longrightarrow Ca(AlSi_2O_6)_2 + 2Na^+$$

Regeneration :

$$Ca(AlSi_2O_6)_2 + 2Na^+ \longrightarrow 2NaAlSi_2O_6 + Ca^{+2}$$

The above two reactions are actually reversible. The direction of the reaction can, therefore, be controlled by eighter excess of Ca^{+2} or Na^+ :

$$Na\text{—Zeolite} + Ca^{+2} \rightleftharpoons Ca\text{—Zeolite} + 2Na^+$$

Zeolite removes both carbonate and non-carbonate hardness and can last for a long time.

(6) ***Synthetic Ion-exchangers*** : Synthetic ion-exchangers of organic and inorganic origin have been developed which remove both cations and anions from hard water. The process of removing both the cations and anions from water by ion-exchangers is known as *demineralization*. Water is thus demineralized with the help of a combination of cation and anion exchangers. Thus, the cation exchanger containing $-SO_3H$ groups in the giant molecule exchange with metal ions in water (R represents the resin matrix) :

$$R\text{—}SO_3H + Ca^{+2} + SO_4^{-2} \longrightarrow (R\text{—}SO_3)_2Ca + 2H^+ + SO_4^{-2}$$

To remove H^+ ion it is passed through a resin bed which removes both H^+ and SO_4^{-2} ions, e. g., polymers having basic amino group :

$$2R\text{—}NH_2 + 2H^+ + SO_4^{-2} \longrightarrow (R\text{—}NH_3)_2SO_4$$

$$R\text{—}NH_2 + H_2O \longrightarrow R\text{—}NH_3^+OH^-$$

$$\downarrow \; H^+ + Cl^-$$

$$R\text{—}NH_3Cl + H_2O$$

This process compares with that of distillation of water and this is now widely used for laboratory, domestic and industrial uses. Both the ion-exchangers can be regenerated by treatment with acid and basic solution respectively. Thus,

$$(R\text{—}SO_3)_2Ca + H_3O^+ \longrightarrow R\text{—}SO_3H + Ca^{+2}$$

and

$$(R\text{—}NH_3)_2SO_4 + OH^- \longrightarrow R\text{—}NH_2 + SO_4^{-2} + H_2O$$

Thus the ions Ca^{+2} and SO_4^{-2} are swept away from the resins which is again ready for use.

Bacteria, viruses, small organisms and many organic matters are removed by chemical oxidation reactions using CaCl(OCl), NaOCl, Cl_2 and O_3. Much of the suspended matter is removed by using gravel and sand. Very fine particles may be removed by formation of gelatinous or amorphous precipitate which coagulate the particles. $Al(OH)_3$ or $Fe(OH)_2$ are generally used in the forms of combination of $Ca(OH)_2$ and $FeSO_4$. $Ca(OH)_2$ however, may dissolve $Al(OH)_3$.

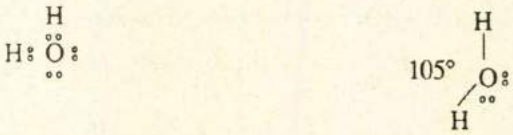
$$Ca^{+2} + 2OH^- + Fe^{+2} + SO_4^{-2} \rightarrow CaSO_4 + Fe(OH)_2 \text{ and}$$

$$3Ca^{+2} + 6OH^- + 2Al^{+3} + SO_4^{-2} \rightarrow 3CaSO_4 + 2Al(OH)_3$$

$$Al(OH)_3 + Ca(OH)_2 \rightarrow CaAl_2O_4 + H_2O$$

Structure of Water Molecule

The properties of water is closely connected with its structure. For example, pure water is a very poor conductor of electricity. This indicates that water molecule is composed of covalent bonds. Water has a high dipole moment. This indicates that bonds between H and O in H_2O are not linear like H—O—H. Because in this case the dipole moment would be negligible or zero. The two hydrogen atoms are actually bonded with oxygen at an angle of about 105° as shown below :—



It is obvious that the charges are unequally distributed in the molecule, oxygen containing more electrons forms the negative part and hydrogen the positive part of the molecule giving a dipole. This explains both dipole moment and dielectric properties of H_2O. The positive and negative parts are joined as part of one molecule and do not move in an electric field as in the case of ions.

X-ray studies indicate that the two hydrogen atoms are situated at the corner of a tetrahedron (distorted) with oxygen at the centre as shown in Fig. 11—?

The oxygen atom having lone pairs of electrons attract the hydrogen atoms of other H_2O molecules and hence the formation of hydrogen bond. Since this process is continued in all the molecules of water forming a giant molecule, water is called an *associated* liquid. This results in the formation of structure in

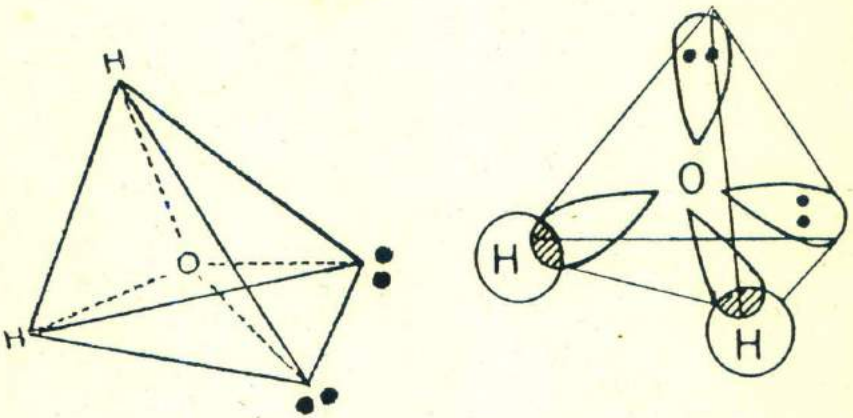
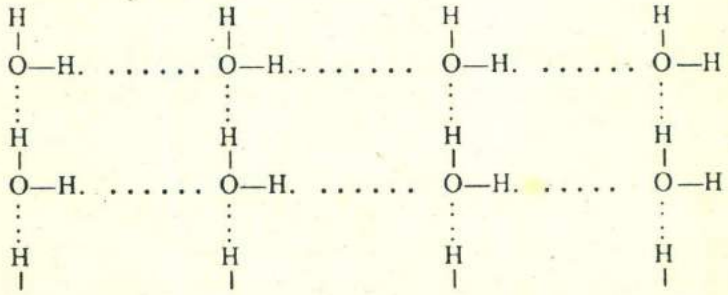


Fig. 11—2. (a) Tetrahedral structure of water molecule. (b) Overlap of hydrogen s orbitals with sp^3 orbitals of oxygen in H_2O.

which each oxygen is surrounded by four hydrogen atoms in three dimensional pattern. A two-dimensional representation is given below. This tetrahedral structure is also shown by solid water (ice).



In ice, combination of the OH_4 tetrahedra through the corners in three-dimensions gives rise to empty hexagonal spaces; because of this, ice has low density and floats on water.

Each oxygen atom in ice crystal is bonded to four hydrogen atoms, two by covalent bonds and two by hydrogen bonds. The hexagonal empty space in ice is shown in two-dimensional pattern in Fig. 11—3.

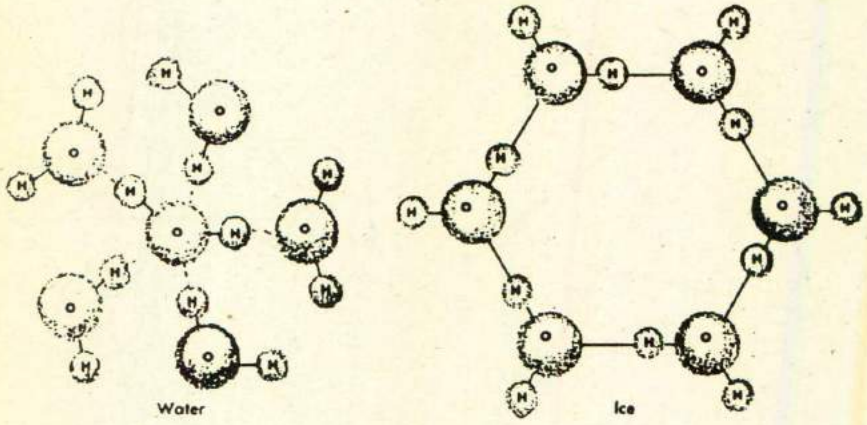


Fig. 11—3. Empty hexagonal space in two-dimensional pattern of ice. Compare with the plane geometry of liquid water.

Chemical Properties of Water

Water has a variety of chemical properties and, in fact, it is more active than what it actually appears.

1. Thermal stability : Water has great thermal stability and is not easily decomposed into its elements. The heat of decomposition of water is very high :

$$2H_2O + 69{,}000 \text{ cal} \rightleftharpoons 2H_2 + O_2$$

and at a temperature of 272°C, only 11.1% of water is decomposed. Compounds which are not easily decomposed into its elements are called thermally stable.

2. Ionization : Water is a poor conductor of electricity because it is only

$$HOH \rightleftharpoons H^+ + OH^-$$

very slightly ionized in which hydrogen and hydroxyl ions have equal concentrations and it is, therefore, *neutral*. Any solution in water having hydrogen ion and hydroxide ion of equal concentrations is also called a *neutral solution*. Solution, in which hydrogen ion concentration is more than hydroxide

ion, is termed as *acidic*. A solution having hydrogen ion concentration less than hydroxide ion is called a *basic solution*.

3. Action of water with elements

(a) With metals : Electropositive metals reacts with water violently. Thus Na, K, Ca etc. give vigorous reaction liberating hydrogen :

$$2Na + 2H_2O = 2NaOH + H_2$$

Magnesium reacts with hot water :

$$Mg + 2H_2O = Mg(OH)_2 + H_2$$

Heavy metals such as Fe, Zn, react with steam when hot :

$$3Fe + 4H_2O \text{ (steam)} = Fe_3O_4 + 4H_2$$

(b) With non-metals : Electronegative elements react with water at ordinary temperature. Thus Cl_2, Br_2 react with water to give—

$$Cl_2 + H_2O = HCl + HClO$$

Fluorine reacts violently with water which actually burns in fluorine liberating O_2 and O_3 :

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

$$3F_2 + 3H_2O \longrightarrow 6HF + O_3$$

Nonmetals, such as carbon, react with steam at red hot condition :

$$C + H_2O = CO + H_2$$

4. Action with oxides : Basic oxides give metallic hydroxides which, when soluble, are strong bases :

$$Na_2O + H_2O = 2NaOH$$

$$CaO + H_2O = Ca(OH)_2$$

Acidic oxides react with water to form acids :

$$SO_3 + H_2O = H_2SO_4$$

$$CO_2 + H_2O = H_2CO_3$$

5. Action with compounds : On crystallisation from aqueous solutions a number of compounds, form hydrates. These are addition compounds with water which may be present in various modes of combination :

$CuSO_4, 5H_2O$ $MgCl_2, 6H_2O$

6. Hydrolysis : The double decomposition of a compound with water is called *hydrolysis*. Thus,

$$AB + HOH \longrightarrow AOH + HB$$

$$PCl_3 + HOH \longrightarrow P(OH)_3 + 3HCl$$

$$Na_2CO_3 + 2H_2O \longrightarrow 2NaOH + H_2CO_3$$

7. Catalytic action of water : Chemical reactions in nature involving decay, fermentation, digestion, growth etc. do not normally take place in absence of water. Intensive drying of some reactive gases makes them devoid of chemical activity. They react only in presence of small quantity of water. Thus intensively dried H_2 and Cl_2 do not react even in sunlight or ultra-violet light. HCl and NH_3 do not react when dry But these gases react readily in presence of a slight amount of water. The exact mechanism of water behaving as a catalyst in chemical reactions has not yet been clearly explained.

8. Water as a solvent : Water is a very common solvent for universal use. But there are numerous compounds which are not soluble in water. The solvent property of water is limited by association due to hydrogen bonding and dissolution of a solute requires rupture of water molecules from this association in order to make room for a solute.

Molecular substances do not go into solution in water. Thus, CH_4, N_2, C_6H_6 etc. are practically insoluble in water; the water structure remains intact in such cases. But solutions of compounds like CH_3OH, C_2H_5OH, $C_6H_{12}O_6$, $C_{12}H_{22}O_{11}$, NH_3 etc. in water are due to strong interactions because of the rearrangements of hydrogen bonds. Thus with NH_3, hydrogen bond is established between the N of NH_3 and the O of H_2O. Similarly, the O of CH_3OH or $C_{12}H_{22}O_{11}$ forms hydrogen bonds.

Most ionic compounds are soluble in water because of the dipole action of water molecule which enables the lattices of the ionic crystals to break apart into

ions, provided the lattice energies in the solids are overcome by the pull. Thus AgF is soluble in water whereas AgCl is not. NaCl is soluble in water whereas $BaSO_4$ is not.

The solubility of ionic solids in water depends mainly on the charges and the size of the ions in the ionic crystals. In fact, the explanation of solubility and insolubility of substances in water medium appears to pose complex questions and no simple satisfactory theory has yet been developed.

HEAVY WATER

Water which is composed of deuterium oxide (D_2O) molecules, is called heavy water.

In 1933, Urey showed that D_2O is present in ordinary water to the extent of 1 part in 6,000 parts.

Water actually contains three types of molecules—HOH, HOD and DOD (ignoring tritium, T).

Preparation of Heavy Water

(1) Electrolysis of water containing N/2 alkali between nickel electrodes gives D_2O. H_2O molecules undergo electrolysis at a faster rate than D_2O molecules :

$$2H_2O \longrightarrow 2H_2 + O_2 \quad \text{fast}$$

$$2D_2O \longrightarrow 2D_2 + O_2 \quad \text{slow}$$

After prolonged electrolysis the residual liquid remaining in the electrolytic cell on distillation becomes enriched in D_2O. Pure D_2O can be isolated in small amount on repeated processing.

(2) Exchange equilibrium process in which commercial hydrogen gas mixed with steam is passed over a catalyst to give D_2O. The process is less costly and is applied in atomic energy work–D_2 in commercial hydrogen is exchanged with steam :

$$D_2 + H_2O \rightleftharpoons H_2 + D_2O$$

On condensing the steam to water it becomes enriched with D_2O. This water is then decomposed by the electrolytic process. The whole process is repeated until nearly pure D_2O (heavy water) is obtained.

Properties : Heavy water has the same appearance as the ordinary water. But there is marked difference between their physical properties.

A comparison of certain physical constants of ordinary water and heavy water is shown in the Table 11.3

Table 11.3. Physical properties of water and heavy water.

Properties		*Ordinary water*	*Heavy water*
1.	Boiling point	100.0°C	101.4°C
2.	Freezing point	0.0°C	3.8°C
3.	Density g/cc. at 20°C	0.9982	1.05
4.	Temperature of maximum density	4°C	11.6°C

Exchange Reaction of Heavy Water

1. Hydrogen in any compound is exchanged with D :

$$NH_4Cl + 2D_2O \rightleftharpoons ND_4Cl + 2H_2O$$

$$2CH_3COOH + D_2O \rightleftharpoons 2CH_3COOD + H_2O$$

2. Pure compounds of D can be prepared by reactions similar to that of water. Thus,

$$CaC_2 + D_2O \longrightarrow CaO + C_2D_2 \text{ (deuteroacetylene)}$$

3. Tracer experiments : Because heavy water, D_2O, is about 10% heavier than H_2O and can be readily distinguished from ordinary hydrogen by mass spectrograph or by weight, heavy water is useful as "tracer" in following the path of chemical reaction and also in physical changes such as digestion and metabolism in the body.

An example of a tracer experiment with D_2O, is the reaction between Zn and HCl solution in water :

$$Zn + 2HCl \xrightarrow{H_2O} ZnCl_2 + 2H_2$$

$$Zn + 2DCl \xrightarrow{D_2O} ZnCl_2 + 2D_2$$

Whether all the H_2 comes from HCl or also from H_2O has been solved by tracing the reaction with D_2O. It has been found that H_2 comes from both HCl and H_2O.

Uses of Heavy Water

Heavy water is largely used to slow down fast neutrons in nuclear reactors and is one of the well-known *moderators* for atomic reactors. It is used for preparation of heavy hydrogen and for tracer studies,

HYDROGEN PEROXIDE

Hydrogen peroxide is one of the compounds containing oxygen-to-oxygen (—O—O—) bonds. Very small amounts of hydrogen peroxide are found in dew, rain water and snow possibly due to cosmic radiation on oxygen.

Preparation of Hydrogen Peroxide

Various methods of production of H_2O_2 have been developed.

1. From Barium Peroxide : When BaO is heated in air, it is converted to BaO_2 which in the hydrated condition forms $BaO_2, 8H_2O$.

BaO_2 is treated with dil. H_2SO_4 solution by which H_2O_2 is formed and remains in solution while insoluble $BaSO_4$ is precipitated out :

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$

H_2O_2 produced is dilute and unstable.

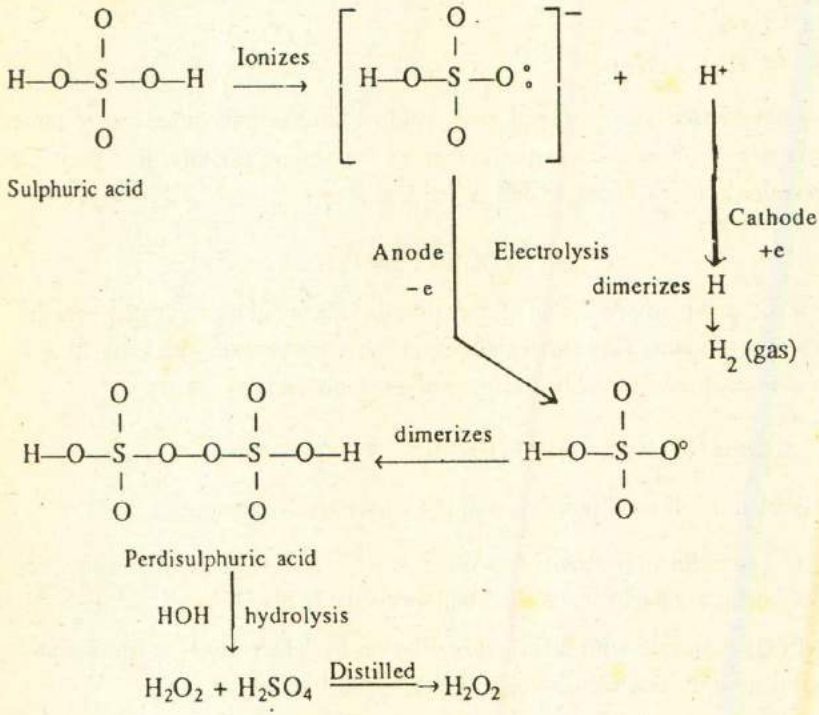
2. From Sodium Peroxide : Sodium peroxide, Na_2O_2, with cold water or dilute H_2SO_4 gives H_2O_2 :

$$Na_2O_2 + H_2O \longrightarrow 2NaOH + H_2O_2$$
$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

Na_2SO_4 is removed by cooling the solution when the salt $Na_2SO_4, 10H_2O$ is crystalised out.

3. Electrolysis of H_2SO_4 : The modern process of producing H_2O_2 is by electrolysis of solution of H_2SO_4 or NH_4HSO_4, Electrolysis of H_2SO_4 solution gives rise to the formation of perdisulphuric acid, $H_2S_2O_8$, at the anode

and H_2 at the cathode. $H_2S_2O_8$ on subsequent hydrolysis gives H_2O_2. The schematic representation of the method is given below :



$$H_2O_2 + H_2SO_4 \xrightarrow{\text{Distilled}} H_2O_2$$

4. From Organic Compounds : Technical production of H_2O_2 from organic compounds have been recently developed. Thus hydroquinone on auto-oxidation in presence of air gives H_2O_2 and quinone. Quinone is again reduced by hydrogenation to hydroquinone and used once again :

$$\underset{\text{Hydroquinone}}{C_6H_4(OH)_2} \xrightarrow[\text{(auto-oxidation)}]{\text{air and water}} H_2O_2 + \underset{\text{quinone}}{C_6H_4O_2}$$

Hydrogenated

Autoxidation of 2-buty anthraquinone is reduced by H_2 (Pd) to the corresponding anthraquinol. Blowing air through the solution of the anthraquinol produces H_2O_2 and liberates anthraquinone for reuse. Propanone is also used.

Properties

Some of the physical properties of H_2O_2 as compared with those of H_2O are given in Table 11.4.

Table 11.4. Physical properties of H_2O_2 compared to H_2O

Properties	H_2O_2	H_2O
Mol. wt.	34	18
m. p. (°C)	0.9	0
b. p. (°C)	151	100
Density g/cc.	1.46	1

Pure H_2O_2 is thermally stable but in presence of impurities, even dust particles, it is dangerously explosive. It is stroed with stabilizer (negative catalyst) such as a weak acid or an organic compound (acetanilide, glycerine). Heavy metal ions act as a positive catalyst and decompose H_2O_2 to $H_2O + O_2$. H_2O_2 is miscible in water, alcohol and ether.

Chemical properties of H_2O_2

The oxidation number of oxygen in H_2O_2 is –1 for each oxygen atom. This is not the normal oxidation number of oxygen in which it is not stable. The more stable oxidation number in which oxygen is stable is 0 or –2. Hence it is expected that H_2O_2 will accept one electron to be present in –2 oxidation state or will lose the one electron to have the 0 oxidation state. Hence H_2O_2 acts both as an oxidizing agent (electron acceptor) and reducing agent (electron donor). The —O—O— linkage is one of the weakest covalent bonds and easily broken or converted to stable oxygen molecule.

H_2O_2 as an oxidizing agent : H_2O_2 acts as an oxidizing agent in all media, i.e., neutral or alkaline or acid solutions. A few examples are given below in the form of equations :

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$

$$H_2SO_3 + H_2O_2 \longrightarrow H_2SO_4 + H_2O$$

$$H_2O_2 + 2KI + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O + I_2$$

$$2HCHO + H_2O_2 \xrightarrow{\text{alkali}} 2HCOOH + H_2$$

$$2K_4Fe(CN)_6 + H_2O_2 + 2H_2SO_4 \longrightarrow 2K_3Fe(CN)_6 + 2KHSO_4 + 2H_2O$$

H_2O_2 as a reducing agent : Reducing actions of hydrogen peroxide take place in acid, alkaline and neutral solutions, and gaseous oxygen is always evolved because H_2O_2 is oxidized by loss of electron to form H^+ ion and O_2. This happens in the case of reactions with powerful oxidizing agents. The following reactions are examples of H_2O_2 as a reducing agent :

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

$$H_2O_2 + Cl_2 \longrightarrow 2HCl + O_2$$

$$2K_3Fe(CN)_6 + 2KOH + H_2O_2 \longrightarrow 2K_4Fe(CN)_6 + 2H_2O + O_2$$

H_2O_2 as a weak acid : Slight ionization of H_2O_2 in water gives the following equilibrium equations :

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \quad \text{(hydroperoxide ion)}$$

$$HO_2^- \rightleftharpoons H^+ + O_2^- \quad \text{(peroxide ion)}$$

The acid character is shown in the evolution of CO_2 from Na_2CO_3 and reaction with $Ba(OH)_2$. It also gives acid salts such as $NaHO_2$, NH_4HO_2 etc. :

$$Na_2CO_3 + H_2O_2 \longrightarrow Na_2O_2 + H_2O + CO_2$$

$$Ba(OH)_2 + H_2O_2 \longrightarrow BaO_2 + 2H_2O$$

Fenton's Reagent : A solution of $FeSO_4$ and H_2O_2, is called Fenton's Reagent. It is used in organic chemistry for catalytic reactions such as polymerisation of acrylonitrile $CH_2 = CH_2—CN$ to its polymers. Neither $FeSO_4$, nor H_2O_2 alone has this property.

Auto-oxidation or disproportionation of H_2O_2 : Hydrogen peroxide oxidizes Mn^{+2} to MnO_2 and also reduces MnO_2 to Mn^{+2} because of self-oxidation of H_2O_2 :

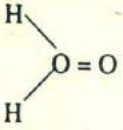
$$H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O \quad - \quad 1.77 \text{ volts}$$

$$H_2O_2 - 2e \longrightarrow O_2 + 2H^+ \quad - 0.69 \text{ volts}$$

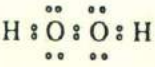
This property is due to the difference in the oxidation potential of the two processes.

Structure of H_2O_2

Formerly H_2O_2 was regarded as having the formula, :



Although some of the properties such as reduction of H_2O_2 are readily explained by the above structure, the experimental evidences show the presence of—O—O—chain. Thus H_2O_2 is represented as H—O—O—H. H_2O_2 is, therefore, known as dihydroxyl. The electronic structure of H_2O_2 is given below :



But the two —OH groups in H_2O_2 are not linear. The atom actually lie in two planes as shown in Fig. 11—4.

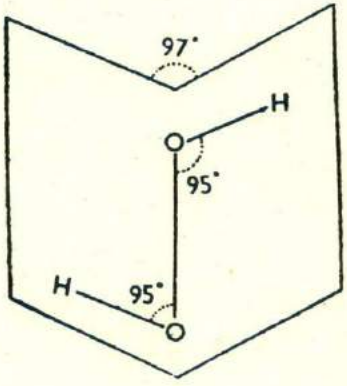


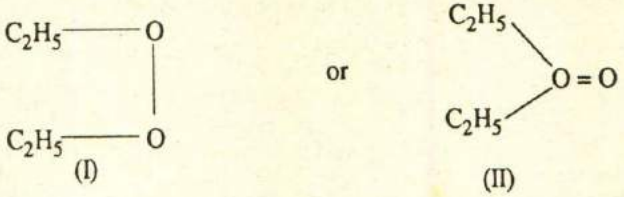
Fig. 11—4. Structure of H_2O_2.

The following reactions prove that H_2O_2 has the structure containing peroxy —O—O— chain.

Diethyl sulphate reacts with H_2O_2 to give diethyl peroxide :

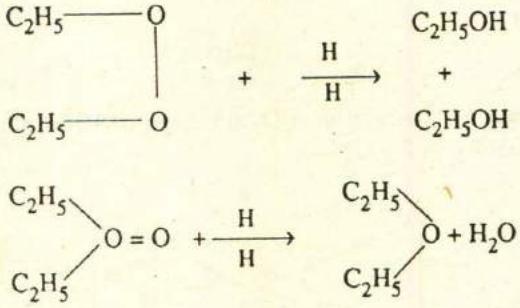
$$(C_2H_5)_2SO_4 + H_2O_2 \rightarrow (C_2H_5)_2O_2 + H_2SO_4$$

$(C_2H_5)_2O_2$ can have two structural formula as given by structures I and II.



(I) (II)

If formula (I) is correct then on reduction with Zn and CH_3COOH it will form C_2H_5OH and if (II) is correct, the formation of ether, C_2H_5–O—C_2H_5, can be visualized.



In actual experiment only ethyl alcohol, C_2H_5OH, is formed. Hence H_2O_2 has the formula H—O—O—H.

Uses of H_2O_2 : (1) A 3% solution of H_2O_2 is used as an antiseptic deodourizer, germicide and for bleaching.

(2) A 30% solution is used as a reagent in the laboratory as an oxidizing agent.

(3) Wool, hair, silk etc. are bleached by H_2O_2.

(4) 90% H_2O_2 solution is used as high explosive and fuels in rockets and guided missiles.

(5) Polymerisation of organic substances containing C = C double bond is achieved by H_2O_2.

QUESTIONS AND PROBLEMS

1. Describe the methods of preparing Atomic Hydrogen and its properties, Explain Nascent Hydrogen, Atomic Hydrogen, Ortho and Para hydrogen.
2. What are :
   (a) Deuterium,
   (b) Heavy water,
3. Write a short note on heavy hydrogen.
4. What is heavy water ? How does it differ from ordinary water ?
5. Discuss the principles involved in the softening of nard water by various methods. Indicate the recent technique developed for this purpose.
6. What are the special properties of H_2O_2 ? How will you establish its structure ?
7. What are the different oxidation states of hydrogen ? Give examples.
8. Discuss some chemical properties of water. Why water is an associated liquid ?
9. What are the different methods for the formation of H_2O_2 ? How do you account for both the oxidizing and reducing properties of H_2O_2 ? Illustrate with examples.
10. Describe the production, reactions and uses of heavy water.
11. Write a note on heavy hydrogen.
12. Write short note on deuterium.
13. Give short description of the preparation and uses of (a) hydrogen peroxide, (b) heavy water.
14. Explain why H_2O is neutral.
15. The molecular hydrides, H_2O and HCl react with each other in the following way:
    $HCl\,(g) + H_2O\,(l) \rightarrow H_3O^+ + Cl^-$
    Explain why the above reaction occurs.
16. Write a chemical equation for the reaction of each of the following oxides with water and specify which are acidic and which are basic.
    P_4O_{10} CsO_2 Li_2O CO_2 BaO
17. Describe how would you convert polluted water into very pure water for use in refined chemical laboratories.

CHAPTER 12

THE PRINCIPLES OF METALLURGY

Metals and Non-metals

The difference in properties between metals and non-metals lies in the fact that atoms of non-metals complete their valence level by sharing of electrons or by transfer of electrons from other atoms. For instance, halogens enter into chemical combination by taking up one electron from another atom or by sharing an electron pair. On the other hand, a metal normally enters into chemical combination by the loss of valence electrons. For instance, sodium loses one valence electron to form compounds. Metallic character decreases and non-metallic character increases with the increasing number of valence electrons. Also the metallic character increases with the increasing number of electron levels.

Looking into the Periodic Table there is no sharp dividing line between metals and non-metals as we progress across the periods of the Priodic Table and also down the groups. Many elements fall on the borderline and show both metallic and non-metallic characteristics. These are known as "metalloids". This class of elements include B, Si, Ge, As, Sb, Te etc. Of the 105 known elements only 17 shows primarily non-metallic character, 8 are metalloids and 70 are metals.

The main differences between the metals arise due to the differences in important physical and chemical properties. Metals are good conductors of heat and electricity and have familiar metallic lustre. Non-metals are poor conductor and have no lustre. Metallic crystals contain metallic bonds between atoms. Non-metals consists of covalent molecules or monoatomic gases. Metals are electropositive and their hydroxides are basic or amphoteric. Non-metals are

electronegative and their hydroxides are acidic. Metals have low ionization potentials and form cations. Non-metals have high electron affinity and form anions. Metals are good reducing agents and non-metals are good oxidising agents.

Occurrence of the Metals

Metals occur in nature mainly in two states :—

*(i) **Free state*** : Less active metals below hydrogen in the activity series sometimes are found in the free state or *native state*. These are Cu, Ag, Au, Pt etc.

*(ii) **Combined state*** : In most cases metals are found in the combined state with other substances which are called *minerals*.

The natural minerals in which metals or their compounds occur in the earth and from which the metals may be extracted economically are known as *Ores*.

Ores generally contain large percentages of rocky and earth materials which are called *gangue*.

Metallurgy

The processes involved in the production of pure metals from their ores are known as Metallurgy. A general review of principles of metallurgy are given briefly as follows :—

The metallurgical operation will necessarily depend on the nature of the ore. The ores always require certain preliminary treatments known as ore dressing. These are :

*(1) **Crushing, grinding and pulverizing of the ore*** : This treatment is necessary for the reactivity and increasing the surface area of the ore for making it more reactive towards chemical attack.

*(2) **Concentration of the ore*** : This is done for removing more of the gangue. The concentration may be achieved by several techniques, such as,

(a) *Washing* : Washing away the lighter particles of gangue with water on slightly inclined shaking table as in the case of gold and tin oxide.

(b) *Magnetic separation* : Metal-bearing ores which are attracted by a magnetic field are separated from non-magnetic impurities by passing the pulverized ore through a magnetic field. Magnetic iron ore may be concentrated in this manner.

(c) Electrostatic separation : The separation by means of electrostatic field may also be employed in some cases as in the case of magnetic separation. The charged particles are separated as in the case of selenium and arsenic.

(d) Froth floatation process : Finely ground ore is mixed with water in a tank to which some oil, such as pine oil, has been added. Air is blown to the mixture producing a great deal of froth. The metal-bearing ore particles adhere to the air bubbles in froth which floats on the surface. The gangues (impurities such as sand, clay, rock) which are wetted by water but not by the oil, sink to the bottom of the tank. The froth containing the ore is removed. This contains the metal in highly concentrated form. This method is particularly suitable for the sulphide ores of Zn, Pb, Cu and also used for carbonates and silicates.

(3) Calcination : The process involves the preliminary heating of the ore in order to convert it to compounds which are more easily reduced to give the metals. Thus, ores containing moisture, hydroxides, carbonates are heated to expel the volatile matter and to decompose the compounds such as carbonate :

$$2\,Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$$

$$CuCO_3 \longrightarrow CuO + CO_2$$

(4) Roasting : In this process the ore is heated to a high temperature in air either alone or with additional substances to effect chemical changes. This involves oxidizing, roasting, blast roasting, chloridising and sulphating roasting. The oxidizing and blast roasting are done to remove S, As, Sb from the ores in a blast of air and convert the ores to oxides :

$$2\,ZnS + 3O_2 \longrightarrow 2\,ZnO + 2\,SO_2$$

Sometimes the ore is converted to chloride by heating with NaCl in presence of air. Thus,

$$Ag_2S + 2NaCl \xrightarrow{O_2} 2\,AgCl + Na_2SO_4$$

Sulphating is the roasting to convert a sulphide ore, such as CuS, to sulphate:

$$CuS + 2O_2 \longrightarrow CuSO_4$$

(5) ***Smelting*** : The process of extraction of the metal in the fused state from the roasted ore is known as smelting. This is based on the chemical reaction involving reduction of the metallic compound. Most metal ores even after roasting contain some gangues. This is removed by adding substances which combine with the impurities. These substances are known as *flux* which combine with the impurities and form fused mass known as *slag* which separates out. Thus, Fe_2O_3 is used as flux in the smelting of Cu, Pb ores. Fe_2O_3 combines with SiO_2 and form $FeSiO_3$ as slag which is easily separated. Similarly, CaF_2 is a good flux in smelting. Other oxides, such as ZnO, BaO, Al_2O_3, MgO are also used as fluxes which combine with SiO_2 to form silicates as slag. The slag is easily removed off from the molten metal because of the difference in the densities.

The methods generally employed for smelting of various ores are :

(a) Oxide ores are generally reduced with C :

$$ZnO + C = Zn + CO$$

$$SnO_2 + 2C = Sn + 2CO$$

$$Fe_2O_3 + 3C = 2Fe + 3CO$$

(b) Other reducing agents such as H_2, Fe and Al are also used;

$$Cr_2O_3 + 2Al = 2Cr + Al_2O_3$$

$$WO_3 + 3H_2 = W + 3H_2O$$

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS$$

(c) Electrochemical methods are used for the halides of Na, K, Mg, Al, Ca etc. Thus Al is produced from Na_3AlF_6 or from Al_2O_3 to which NaF and AlF_3 have been added. The electrochemical process requires certain conditions to be followed rather rigidly. The selection of electrodes, the temperature of fusion, the voltage and current are some of the factors. To lower the fusion temperature and conduct electricity, proper fluxes are added.

(d) Metals occurring in the native state are separated by some convenient methods such as heating the ore and allowing the molten metal to drain away.

(6) ***Hydrometallurgy*** : In this process the metals present in the ore is made to go into aqueous solution due to some chemical changes. The metals is then separated by suitable means. Thus Ag is dissolved in dilute solutions of NaCN in presence of air forming $NaAg(CN)_2$ from which Ag is precipitated out by adding Zn.

(7) ***Refining of metals*** : Smelting process generally gives impure form of metals which require further purification. The contamination generally consists of small quantities of other metals and non-metals such as Si, P, S, C etc. The process of removing the last traces of impurities from the smelted metal is known as refining. Various methods of refining are employed for the purification.

(a) Volatile and low boiling metals such as Zn and Hg are purified by distillation.

(b) By simple oxidation the impurities oxidize away in the molten state when a blast of air is passed in a suitable furnace. Thus S, C, P etc. can be easily removed from metals.

(c) Liquation process is used when the impurities are not easily fusible than the metal. Thus Sn can be fused on an inclined table and thus flows away from higher melting impurities. Similarly, Zn is separated from Pb at the melting point of Zn. The heavier Pb which does not melt at that temperature settles down to the bottom whereas molten Zn floats on top and is separated.

(d) Electrolytic method is the most used method for the refining of many metals. The impure metal is made the anode and the pure metal the cathode of an electrolytic cell. Thus Cu, Au, Zn etc. are refined.

The different types of furnaces and extraction appliances which are used in smelting process have been described at the appropriate places in this book. Some of the well-known furnaces are : (i) kiln, (ii) blast furnace, (iii) reverberatory furnace, (iv) muffle furnace, (v) tube furnace, (vi) rotary kiln furnace, (vii) electric furnace of various designs, (viii) various types of electrolytic cells.

QUESTIONS AND PROBLEMS

1. Describe with examples, the general principles underlying the extraction of metals from their ores.
2. What are the properties which distinguish metallic elements from non-metallic elements ?
3. Explain the concentration of sulphide ores by floatation process.
4. Write notes on the following :—
   (a) Smelting,
   (b) Hydrometallurgy,
   (c) Roasting of ores,
5. What are the process for concentrating the ores from the natural minerals ?
6. Why is it necessary for the purification of the metals extracted from the ores? Discuss some of the methods of refining.
7. Describe the differences between metals and non-metals.

CHAPTER 13

STUDY OF GROUP CHEMISTRY OF ELEMENTS

(General Remarks)

The study of the chemistry of elements in a group may appear to be rather cumbersome and difficult particularly when the student is required to enumerate the points of comparison and contrast between two elements or sets of elements in the same group or of different groups. But the vast informations of the descriptive chemistry of groups of elements can easily be grasped if it is remembered that the physical and chemical properties of elements depend mostly on the electronic configurations. This is more readily understood by the elementary students who can easily correlate the facts with the electronic arrangements in the atoms of the group of elements under study. However, a knowledge of the important facts regarding the group chemistry of the elements is also necessary for correlation. This can be gathered from a general idea.

For instance, the mode of occurrence in nature of a particular element or group of elements may be easily understood from the point of view of electronic structures. The alkali metals cannot exist in nature in the free state, so also halogens. A student who is familiar with the chemical reactivity of these groups of elements can easily understand why these elements do not occur in nature in the free state. It is to be remembered that elements can occur in nature (in the atmosphere, in the earth and in the sea). On earth, the animal kingdom, the plant kingdom and the minerals are the possible sources of elements. Which element is found in what sources is governed mainly by its chemical reactivity which in turn is governed by the electronic structure. Water soluble salts, such as sodium chloride, magnesium chloride etc.are abundantly available in the sea water because these might have been washed down by water and ultimately have

become concentrated in the sea water. Most of the transition metals occur in the mineral kingdom because these are stabilised in combinations as oxides, sulphides, silicates etc. Carbon compounds obviously will be found in the plants and the animals. Thus the mode of occurrence can be correlated from the properties of the elements and their electronic structures.

The study of group chemistry of elements can be simplified by keeping in view the following points of discussion :—

I Grouping of the elements in the Periodic Table and the electronic structures.

II Discussions of the physical properties.

III Discussions of the chemical properties.

IV Extraction processes.

V Some important compounds.

VI Uses and industrial applications.

The descriptive chemistry of an individual element also follows a similar method of study comprising the above mentioned points. A short discussion of the important points are given below.

I Grouping in the Periodic Table and the Electronic Structure

The set of given elements belong to a particular group in the Periodic Table and this must be mentioned at the very outset in the descriptive chemistry. Their electronic structure will make it easier to give a description of the main features of the properties of the elements and hence this must be illustrated at this stage.

II Physical Properties

(1) The main points to be touched regarding the physical properties may have some obvious bearing with the electronic structure. The physical state or the state of aggregation has to be mentioned. The element or elements may be solid or liquid or gaseous, or some may be solid, some may be liquid or gaseous at the ordinary temperature, and there may be some apparent reasons for the same. If possible, an explanation may be given as to why the element or elements exist in one of the three states at the ordinary temperature. Mention here must be made regarding their metallic, non-metallic or metalloidic characters

if the elements are solid at ordinary temperatures. Colour, odour, hardness and density, may also be mentioned, if necessary ; otherwise, may be omitted.

It must be remembered that it is not necessary to give values for the physical properties and constants. But the gradation and a rough idea regarding the variations in physical properties may be illustrated in a qualitative manner. This again follows from the electronic structures to a great extent as given in Chapter 4.

(2) Atomic sizes, ionic radii and ionization potential can be discussed in relation to the electronic arrangements. As mentioned before, these considerations have great influence on the chemical behaviour of the elements in a group and the overall structures of the molecules.

(3) The melting and the boiling points of the elements and their compounds depend on the bonding characteristics and if they are explained from this point, it will give better understanding. For instance, alkali metals from Li to Cs have gradually low melting points whereas halogens from F_2 to I_2 exhibit the reverse phenomena and pass from gaseous state to solid at ordinary temperature.

(4) Solubility or insolubility in water and other well-known solvents, if necessary, may be mentioned. If there is a chemical reaction with water it should be mentioned in the discussions under the chemical properties. The solubility, apart from other characteristics, gives some idea about the bonding system in the element and their compounds.

(5) In the case of metals, conduction of heat and electricity may be mentioned in relation to the electronic configuration. Metals generally conduct electricity whereas non-metals are non-conductor. The presence of mobile electrons in metals arising out of the valence electrons gives an idea about the electrical condictivity.

(6) If the elements have characteristic spectra with striking features involving particular electronic arrangements, a mention of this point will be justified. For instance, the importance of spectral studies in the case of inert gases and other familiar group of elements are to be discussed.

(7) Special physical properties, such as allotropic forms, polymorphism, specific heat, crystal structures may be mentioned where necessary. As in the case of carbon, phosphorus, sulphur groups these features are of importance.

III Chemical Properties

The description of chemical properties of element in a group may deal with the following points :—

(1) ***Valence state:*** (Oxidation states) and the bonding system of the elements can be discussed with examples. Here again, the complete understanding of the electronic structure is a great help to develop this point which must be illustrated with examples. The oxidation state of alkali metals is +1, whereas in the case of the nitrogen group a number of oxidation states are possible. Similarly transition metals show variable oxidation states. These can be readily explained if the electronic structures of the elements are known.

(2) ***Action of air*** : A discussion regarding the stability or instability of the elements in air is quite interesting. Since air contains oxygen, nitrogen, moisture and carbondioxide etc., a description of the action of air on the elements naturally entail the effect of these agents at the ordinary condition and other conditions. For instance, burning of alkali metals and phosphorus in presence of air due to the combination with oxygen, formation of an oxide or carbonate films on the surface of metals or rusting of iron in moist air, are some of the examples. Everlasting brightness of gold and platinum indicates their inactivity with air. These facts are interesting and invoke inquisitiveness in the minds of students when the explanation of these facts are correlated with atomic structure.

(3) ***Action of water*** : Some elements react vigorously with water and some are attacked very slowly. The chemical reaction with water can be discussed from the point of view of the electronic structure. Water may give various types of reactions with elements. Hydrolysis may occur in which case the elements can combine both with H and OH parts of H_2O forming a hydride and a hydroxide of the element as in the case of chlorine :

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

The water molecule may be reduced by an element thereby liberating free hydrogen gas if the reduction potential favours displacement reaction :

$$2\,Na + 2\,H_2O = 2\,NaOH + H_2$$

Some elements decompose water at red heat. Why do such phenomena occur?

(4) Action of acids: In this connection, actions of more well-known acids, such as HCl, HNO_3 and H_2SO_4 may be mentioned. Only the cases which require reference to special acids, may be included. In some cases the concentration of the acids and the temperature of reactions may be discussed. The special case of nitric acid being an acid and also an oxidising agent may be touched particularly in the case of its reaction with metals.

(5) Action of alkalis: The reactions of both the caustic alkalis and ammonium hydroxide may be discussed if applicable. Here also the state and concentrations of alkali solutions produce different results with different elements. For instance, some metals may not react with alkali at all (Au and Pt) either in the solid or in solutions at any temperature. Metals like zinc and aluminium dissolve in alkali solution evolving hydrogen. The halogens produce various oxidising products in alkali solutions depending upon the concentration.

(6) Action of halogens: Halogens (particularly F, Cl, Br) being a group of most reactive substances provide an opportunity to discuss the formation of halides of the given group of elements by direct reactions. The reactions with halogens throw a great deal of light on the reactivity of the elements under discussion and their normal oxidation states. The formation of halides of the elements having a general formula MX, MX_2, MX_3, M_2X_3, MX_4 etc. represent reactions between groups of elements which are either very uniform as in the case of alkali and alkaline earth metals or show different oxidation states as in the case of transition metals.

(7) Action of hydrogen : The activity of an element or a group of elements presents an interesting study because of the state in which hydrogen enters into combination. In the case of alkali and alkaline earth metals, the product known as hydrides, contain hydrogen as H^- ions and are crystalline solids. With group III elements, particularly boron, a very large number of complex polymer hydrides are generally formed. With transition metals they form interstitial types of compounds and in some cases hydrogen is absorbed in considerable quantity as in the case of Pd, Pt etc. With halogens it forms the

well-known hydracids in which hydrogen may be regarded as H^+ ions particularly in aqueous solutions as H_3O+.

(8) Special properties : Under this discussion other interesting reactions or formations of particular compounds peculiar to the group of elements may be mentioned. This may include formation of complex compounds as in the case of transition metals, departure from the general behaviour as in the case of similarity of Li and Mg, Be and Al etc.

IV Extraction Processes

The extraction processes and isolation of an element or group of elements in the Periodic Table naturally depend upon the mode of occurrence. It must be remembered that the extraction process from the naturally occuring materials require the understanding of the electronic structure of the element under consideration. Some of the metals, such as silver, gold, mercury, platinum and also the inert gases, occur free in nature. Others are found in the combined state generally known as minerals. A mineral which contains sufficient quantity of an element from which it can be readily and profitably extracted is known as an ore. The ore of an element has the element in combination with other elements in which it is most stable. Alkali metals are stable as halides and occur in nature as halide. Most metals occur as sulphides or oxides as well as carbonates, silicates and phosphates. These may be simple or complexed with other ores and minerals. The geological factor such as aging under pressure markedly decreases the chemical reactivity of minerals and ores and requires chemical treatment for *opening up* of the ores for the extraction of the particular element. Hence a short discussion of the principle involved in the process of extraction gives a good point in the description of the chemistry of an element or a group of elements.

V Compounds

Some important and well-known compounds may be briefly described giving special features as regards their formation, properties, structures and applications.

VI Uses and Industrial Applications

The study of chemistry as a science embodies the knowledge of elements and their compounds for useful purposes. This is the very basis of our civilization.

Hence a mention regarding some useful applications makes an interesting description.

CHAPTER 14

THE MOST BASIC METALS : THE ALKALI METALS

(The Elements of Group IA)

Li—Lithium,	Na—Sodium,	K—Potassium
Rb—Rubidium,	Cs—Cesium,	Fr—Francium.

Of all the elements, the elements of Group IA, generally known as the alkali metals, have the simplest chemistry because these elements have a single electron in the outermost energy level. The inner electrons in the alkali metals screen the bulk of the positive charge on the nucleus so effectively that the single electron moves under the influence of a positive electric field resembling that of a hydrogen atom. The chemistry of the alkali elements is, thus, largely dependent upon this single electron.

The electronic structure : The electronic structures of the alkali metals are given in Table 14.1.

Table 14.1. Electronic structures of alkali metals.

At No.	*Element*	*Electronic structures*	*Valence electron*
3	Li	He core, $2s^1$	$2s^1$
11	Na	Ne core, $3s^1$	$3s^1$
19	K	Ar core, $4s^1$	$4s^1$
37	Rb	Kr core, $5s^1$	$5s^1$
55	Cs	Xe core, $6s^1$	$6s^1$
87	Fr	Rn core, $7s^1$	$7s^1$

It is to be remembered that an **s** electron having n=1 has one spherical zone of maximum charge density in the electron cloud and n=2 has two spherical zones and so on. Each horizontal row gives symmetry of the electron cloud corresponding to $l = 0, 1, 2, 3$ or **s, p, d** and **f** electrons.

It can be seen from the electron structure diagram in Table 14.1 that each alkali element has a solitary unpaired electron in the outermost shell. As the atomic number increases from Li (3) to Fr (87) thereby building the positive charges on the nucleus, the electrons of the inner completed shells are pulled very close to the nucleus. The completed shells of negative electricity are very effective in neutralizing the attraction of the positive nucleus on the solitary electron in the outermost energy level. The outermost shell is, therefore, very diffuse and the electron can be easily removed from the atom.. It is this factor which is largely responsible for the chemistry of alkali metals.

General Characteristics

Physical properties : Some of the physical properties of the alkali metals are given in Table 14.2 which are explained from the point of view of the electronic structure.

Table 14.2. Physical characteristics of alkali metals.

Physical properties	*Li*	*Na*	*K*	*Rb*	*Cs*	*Fr*
At. No.	3	11	19	37	55	87
At. Wt.	6.94	22.997	39.009	85.48	132.91	223
Atomic radius (Å)	1.5	1.86	2.27	2.43	2.62	2.7
Ionic radius (Å)	0.60	0.95	1.33	1.48	1.69	—
Ionization potential (ev)	5.4	5.1	4.3	4.2	3.9	—
Electronegativity	1.0	0.9	0.8	0.8	0.7	—
Density at 20°C(g./cm.^{3})	0.534	0.97	0.86	1.53	1.90	—
Melting point (°C)	186	97.6	62.3	38.5	28.5	—
Boiling point (°C)	1336	880	760	696	670	—
Electrode potentials M/M^+ (volts)	3.02	2.71	2.92	2.99	3.02	—

The above physical properties may be linked with the loose bonding of the single valence electron in the alkali metals. The values of ionization potentials indicate that it requires only 5.4 ev to remove $2s^1$ electron from Li (as compared to 13.6 ev required to remove $1s^1$ electron from H). The ionization energy decreases from Li to Cs because of the increasing shielding effect of the inner core of completed shell on the nuclear charge of the atoms. Thus, the case with

which the valence electron is lost, increases with the increasing atomic radius since the valence electron occupies greater volume as the atomic number increases.

The electronegativity values give a similar measure of this tendency and reflect the same trend. Alkali metals are, therefore, the most electropositive elements having very low electronegativities. It is to be remembered that the loss or removal of the outer electron leaves the atoms in the form of alkali metal ions. The sizes of the ions indicate that the reduction from the neutral atomic radii is quite considerable because of the looseness of the solitary outermost electron. As a group, the alkali metals have greater atomic radii and lower ionization potentials than any other group of elements.

In metals it is the valence electrons that hold the individual atoms together in the solid. The combined neutral atoms have the outer electron clouds merged with that of the neighbours. In fact, the metals present a picture of ions as a close-packed arrangement immersed in a sea of valence electrons. In the alkali metals this sea of valence electrons is very diffuse and the merged electron clouds constitute a weak binding in the solid. The valence electrons move freely from one atom to the other. The relatively weaker binding in the solid alkali metals gives rise to the low melting and boiling points, softness of the metals and makes it easy to compress. The free motions of the valence electrons give rise to the high electrical conductivity (low electrical resistance) and high lustre of the metal surface is due to easy excitation of the electrons by ordinary light which is reflected (photoelectric effect). The alkali metals also give characteristic visible colouration to the flame.

Chemical properties : Because of easy removal of the single valence electron, the alkali metals invariably exhibit oxidation number of +1 in their compounds. Removal of a second electron from the completed shell is exceedingly difficult. This factor is responsible for the strongly developed ionic character of alkali metal compounds.

Because the alkali metals give up electrons so readily, these function as excellent reducing agents.

(a) Action of air : All the alkali metals except Li readily react with the oxygen of the air and tarnish quickly. There is gradation in the reactivity and the products of reaction have different composition.

Lithium reacts with oxygen of air in heated condition forming Li_2O. Sodium reacts slowly at room temperature and vigorously on heating to form peroxide, Na_2O_2. Potassium reacts vigorously at room temperature to give superoxide, KO_2, having O_2^- anion.

Rubidium and cesium react so rapidly with oxygen at room temperature that they are inflamed and yield superoxides, RbO_2 and CsO_2. Freshly prepared or cut surfaces of alkali metals are silvery white, but on exposure to the air they are coated with oxide film and the metallic lustre is destroyed (tarnished).

(b) Reaction with water : It is a well-known fact that alkali metals, such as sodium, react very vigorously with water forming hydrogen gas and an alkaline solution. The outermost single loose electron in the alkali metals is responsible for this vigorous reduction of water. Apparently, lithium appears to react with water less vigorously, but it is due merely to a physical condition although the energy released during the reaction with water is far greater than any other alkali metal. The physical factor for less vigorous reaction of lithium is the high melting point, above 100°C (186°C). The low melting points of other alkali metals actually make them melt due to the heat of reaction with water and hence the reaction is very vigorous.

But the case of lithium is different and lithium is actually the best reducing agent although cesium is the best electron donor. This is because of the fact that the standard electrode potential (E°) of lithium is as effective as that of cesium although the ionization potential of lithium is higher than any other alkali metals.

In order to understand the significance of the above statement the values for the ionization potential (energy needed to remove a single outer electron from the atom to form an ion) and the standard electrode potential (energy involved in removing an electron and forming a hydrated metal ion) of alkali metals are given in Table 14.3

Table 14. 3. Ionization potentials and standard electrode potentials of alkali metals.

Ionization potentials	*(ev)*	*Standard electrode potential*	*(volts)*
Li	5.4	Li/Li^+	3.05
Na	5.1	Na/Na^+	2.71
K	4.3	K/K^+	2.92
Rb	4.2	Rb/Rb^+	2.93
Cs	3.9	Cs/Cs^+	2.92

The standard electrode potentials of alkali metals show no gradation in values and is not gradually decreased as in the case of the ionization potential. As has been mentioned, the standard electrode potential is related to the amount of energy involved in removing an electron from a metal and forming a hydrated metal ion and hence this is a composite property and takes into account several factors.

Born-Haber Treatment : The factors which are involved in the formation of a hydrated metal ion from a solid metal are given by the well-known Born-Haber Treatment. A simplified version of the Born-Haber cycle in the case of energy involved in forming hydrated metal ion takes into account the following factors.

(1) Energy required for the breaking up of the solid (metal crystal structure) into individual atoms designated as sublimation energy (S).

(2) Energy-required for the atoms to become ions designated as ionization energy (I).

(3) Energy released when the ions become hydrated and designated as hydration energy (-H).

(4) Energy involved in randomness of the reaction for hydration of the metal ions since the water molecules tend to surround each metal ion and the freedom of motion of the ion is reduced. This is designated as entropy effect (Δ S) and is negligible in the case of alkali metals.

$$\underset{\text{crystal (solid)}}{M} \xrightarrow{S} \underset{\text{Free atoms}}{M} \xrightarrow{I} \underset{\text{Free ions}}{M^+} \xrightarrow{-H} \underset{\text{hydrated ion}}{M^+(H_2O)_n}$$

The electron lost during the ionization is responsible for the very exothermic reaction represented by,

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$$

Hence the total reaction is actually,

$$2M + 2H_2O \longrightarrow H_2 + 2M^+ + 2OH^-$$

The total energy required by Li, Na and Cs for conversion from metal to hydrated ions are given in Table 14.4.

Table 14.4. Energy of hydration of some alkali metals for $M^+(H_2O)_n$.

Metals	*S* *Kcal*	*I* *Kcal*	*−H* *Kcal*	*Net energy* *Kcal*
Li	38	124	−123	39
Na	26	119	−97	48
Cs	19	90	−63	46

S = Sublimation energy, *I* = ionization energy, *−H* = Hydration energy.

Thus a small ion, such as lithium, attracts the dipole of water more strongly and is more readily hydrated as compared to cesium. Hence the very high energy of hydration of the tiny lithium makes lithium a better reducing agent than cesium.

(c) Reaction with acids : The alkali metals react violently with dilute acids.

$$2Na + 2H^+ = 2Na^+ + H_2$$

(d) Reaction with hydrogen : The alkali metals combine directly with hydrogen on gentle heating forming crystalline colourless compounds known as alkali metal hydrides. These are ionic compounds composed of alkali metal positive ion (M^+) and negative hydride ion (H^-). Thus in general,

$$2M + H_2 = 2\,MH$$

$$2Na + H_2 = 2\,NaH$$

Lithium hydride and sodium hydride are well-defined compounds and have high melting points. The presence of a negative hydrogen ion is proved by

electrolysis of molten alkali metal hydrides, when hydrogen is released at the anode. These hydrides are easily decomposed by water producing hydrogen which is double the quantity contained in the hydride.

$$NaH + H_2O = H_2 + NaOH$$

These alkali metal hydrides are of great practical importance as hydrogenating agents, deoxidizing agents in the manufacture of steel and as possible rocket fuels.

(e) **Reaction with halogens** : All the alkali metals react violently with the halogens to form the important compounds known as alkali halides. The reaction takes place with almost explosive violence which is the result of the rapid transfer of an electron from alkali metals to the halogen atom. The reaction follows the equation :

$$2M + X_2 = 2MX \qquad X = F, Cl, Br, I$$

But it has been noted that during the reaction free halogen atoms are also formed. Thus,

$$Na + Br_2 = NaBr + Br$$

Due to the explosive nature of the reaction, alkali halides are never prepared by the above direct reactions. However, the reaction between the alkali metal hydroxide and halogen acids may be used for the formation of alkali metal halides in aqueous solutions.

The alkali halides are colourless solids, readily soluble in water and are of important applications.

(f) **Reaction with nitrogen** : The alkali metals form nitrides, M_3N, when gently heated in presence of nitrogen particularly in an electric discharge tube :

$$6Na + N_2 = 2Na_3N$$

The nitrides are readily decomposed in presence of water giving off ammonia:

$$Na_3N + 3H_2O = 3NaOH + NH_3$$

The azides of alkali metals are also formed having general formula MN_3. These detonate very easily and are decomposed in vacuum when gently heated giving off nitrogen :

$$NaN_3 \xrightarrow{200°C} Na_3N + N_2$$

It is to be noted that the alkali metals show a much closer similarity to each other than the elements of any other group which is attributed to the presence of single valence electron which mainly determines the chemical characteristics of these elements.

Occurrence of the Alkali metals

The alkali metals always occur in nature as compounds having ions with a single positive charge. Because the compounds are generally soluble in water, they are found in solution, in the ocean, in the lakes and in underground water. They are found in the solid state in dried-up lakes or ocean beds and in underground deposits. Lithium, potassium and cesium also occur in silicate minerals, such as orthoclase, $K_2Al_2Si_6O_{16}$, spodumene, $LiAl((SiO_3)_2$, pollucite, $H_2Cs_4Al_4(SiO_3)_9$ etc. Lithium also occurs in mineral water and plants such as tea and tobacco leaves. Potassium is found in plants, and water-hyacinth also contains quite appreciable amount of K.

Metallurgy of Alkali Metals (Extraction)

Because of the great reactivity and reducing properties of alkali metals they cannot be prepared by chemical reaction from their compounds in large quantity. The pure alkali metals are obtained by electrolysis of their molten salts or hydroxides. Sodium is produced in commercial scale while lithium metal has shown marked increase in production in recent years.

SODIUM : Sodium is produced by electrolysis of fused sodium chloride mixed with sodium carbonate or calcium chloride to lower the melting point of the salt from 801° to 600°C. The cell used now-a-days for the electro-metallurgy of sodium is the Down's cell, shown in Fig. 14—1.

The electrolyte is a mixture of sodium chloride and calcium chloride. The graphite anode is encircled by an iron or copper cathode and the two are separated by an iron screen partition. This arrangement allows the electric current to pass,

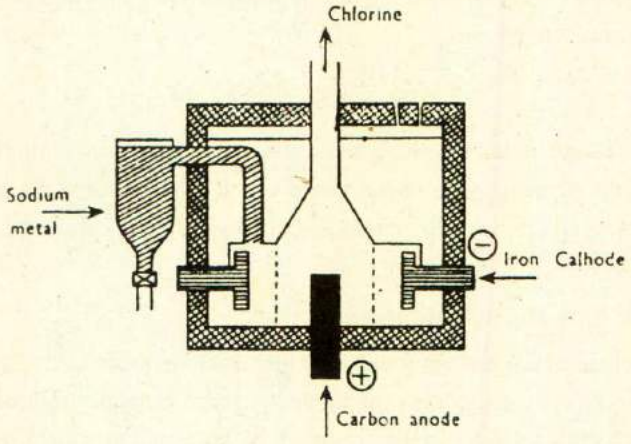


Fig. 14—1. Down's cell for sodium production.

but keeps the sodium and chlorine from coming in contact after they have been set free at the cathode and anode respectively. The fused sodium rises in a special compartment from which it may be drawn off, and dry chlorine is collected in the dome above the anode. Because of low consumption of energy the Down's process has largely replaced the Castner process using fused sodium hydroxide as the starting electrolyte.

LITHIUM : The silicate or phosphate minerals of lithium require chemical processing in order to convert it into lithium chloride which is then used for the extraction of lithium. The chemical processes of the minerals involve several techniques such as digestion with H_2SO_4 or K_2SO_4 to produce Li_2SO_4 which is converted to LiCl.

The extraction of lithium is carried out from fused lithium chloride in a similar manner as in the case of sodium.

POTASSIUM, RUBIDIUM AND CESIUM : Potassium is produced only in small scale from carnallite. In the case of potassium, the potassium hydroxide is a more convenient electrolyte than potassium chloride, because it has a low melting point of 360°C as compared to KCl, 776°C.

Metallic rubidium and cesium are not produced for commercial purposes.

FRANCIUM, element 87,is radioactive and has been isolated from the disintegration of an actinium isotope Ac^{227}. Francium is very unstable with a half-life of only 21 minutes and has the same chemistry as that of cesium and is the heaviest alkali metal. Actinium 227 decays with the emission of β–particles forming Th^{227}. But 1% of Ac^{227} disintegrates with the emission of α–particles forming element Fr(87) :

$$_{89}Ac^{227} \longrightarrow \beta^- + {}_{90}Th^{227}$$

$$_{89}Ac^{227} \longrightarrow {}_2He^4 + {}_{87}Fr^{223}$$

Uses of the alkali metals

Lithium is the lightest of all solid elements. In recent years considerable advance has been made in the applications of lithium. Lithium is extensively used for the purification of inert gases and in refining of metals, such as Cu and Ni, which are purified of impurities, such as oxides, sulphides etc. Lithium acts as a deoxidizer. Lithium is used in organic synthesis, e. g., preparation of ketones. Alloys of lithium have unusual properties. Pb-Li alloy is used as a bearing material. Li-Mg and Li-Zn alloys have high tensile strength and resistance to atmospheric corrosion. Scleron (Li-Zn alloy) compares with mild steel in tensile strength and elasticity.

Sodium is extensively used in industries and as reducing agents in the production of metals, such as titanium and zirconium from their chlorides and oxides. It is used in the production of Na-Pb alloys which are in turn used in the production of tetraethyl lead, a gasoline additive, from ethyle chloride. Sodium metal is used as catalyst in the production of organic compounds and also for organic analysis. It is also used for heat conduction in atomic reactors and aircraft engines. Sodium is used in sodium vapour lamps which gives characteristic yellow light for lighting highways. The largest uses of sodium are in manufacture of compounds, such as sodium peroxides, sodium cyanide, amide etc. which cannot be made directly from sodium chloride. Sodium and other alkali metals are used in photoelectric tubes.

Potassium has limited use. a sodium-potassium alloy provides a convenient way of handling Na or K and is used in organic reactions and for heat transfer medium in industry. A 50—50 parts Na—K alloy is liquid at ordinary temperatures. Cesium is also used in photoelectric cells.

Alkali metals dissolve in liquid ammonia giving blue solutions containing ammoniated electrons. These solutions are good reducing agents.

Some Important Compounds of Alkali Metals

Alkali metals form well-defined compounds. Almost all of them are colourless and soluble in water except in some cases. The coloured anions, such as dichromate, permanganate, cobaltinitrite, nitroprusside etc., produce coloured salts of alkali metals. Some alkali metal salts, particularly those of lithium, such as Li_2CO_3 and Li_3PO_4, are insoluble in water.

Compounds of Lithium

All lithium salts are obtained from the lithium minerals in various ways. The minerals are processed to obtain Li_2CO_3 or LiCl. These are converted into other lithium compounds by chemical reactions.

Lithium fluoride, LiF : This is obtained by treating a soluble lithium salt, such as LiCl, with ammonium fluoride. LiF being sparingly soluble is precipitated out :

$$LiCl + NH_4F = LiF + NH_4Cl$$

LiF is not hygroscopic. This is used as a flux in electrometallurgy and as opacifying agent in ceramic and enamel industries.

Lithium chloride, LiCl : This is produced when lithium carbonate or oxide is treated with HCl. LiCl is one of the most hygroscopic substances and it is soluble in organic solvents, such as alcohols, ether and pyridine. Due to its bygroscopic nature LiCl is extensively used as dehumidifier in air-conditioning plants. Lithium bromide LiBr is also used as dehumidifier and air conditioning.

Lithium sulphate, Li_2SO_4 : Tihis is formed from Li_2CO_3 dissolved in H_2SO_4. It is readily soluble in water and also in alcohol unlike other alkali metal sulphates.

Lithium oxide, Li_2O : This is obtained by heating Li_2CO_3, $LiNO_3$ or LiOH in presence of hydrogen.

Lithium hydroxide, LiOH : This is obtained by dissolving Li_2O in H_2O when LiOH is formed, LiOH is also obtained when Li_2SO_4 is treated with a solution of $Ba(OH)_2$:

$$Li_2SO_4 + Ba(OH)_2 = 2LiOH + BaSO_4$$

LiOH crystallises from solutions as $LiOH.H_2O$ and has strong basic character.

Lithium peroxide, Li_2O_2 : Lithium peroxide is formed by drying the precipitate of Li_2O_2. $H_2O_2.3H_2O$ which is obtained by adding H_2O_2 and alcohol to a solution of LiOH. The drying is done over P_2O_5.

Lithium nitride, Li_3N : Metallic Li combines slowly with N_2 at room temperature but burns brightly when heated in N_2 forming Li_3N. It is the only alkali metal which combines with nitrogen directly. It resembles with Mg in forming Mg_3N_2. Li_3N is decomposed by H_2O.

$$2Li_3N + 6H_2O = 6LiOH + 2NH_3$$

Li_3N is used as a catalyst in the manufacture of synthetic ammonia.

Lithium phosphate, Li_3PO_4 : This is obtained as precipitate when Na_3PO_4 is added to a soluble lithium salt, e.g., LiCl. This is also obtained by the reaction of H_3PO_4 with Li_2CO_3 :

$$3LiCl + Na_3PO_4 = Li_3PO_4 + 3NaCl$$

$$3Li_2CO_3 + 2H_3PO_4 = 2Li_3PO_4 + 3CO_2 + 3H_2O$$

Li_3PO_4 is almost insoluble in water and, therefore, differs from the corresponding compounds of other alkali metals which are soluble. In this way, it resembles alkaline earth phosphate.

Lithium carbonate, Li_2CO_3 : This is also almost insoluble in water and thus differs from other alkali carbonates and resembles alkaline earth carbonates. Li_2CO_3 is obtained by the addition of ammonium carbonate to any soluble lithium salt in presence of ammonia :

$$2LiCl + (NH_4)_2CO_3 = Li_2CO_3 + 2NH_4Cl$$

Lithium carbonate is used in glass industry.

Li_2CO_3 dissolves in a solution of CO_2 giving lithium bicarbonate, $LiHCO_3$, which is more soluble in water than Li_2CO_3 like $Ca(HCO_3)_2$:

$$Li_2CO_3 + CO_2 + H_2O = 2LiHCO_3$$

The solution of $LiHCO_3$ is known as Lithia water, and is used in medicine as a remedy for gout because lithium urate formed in the body is fairly soluble in water and is excreted with urine (for expelling uric acid from human system).

Lithium hydride, LiH : This is formed by direct combination of the elements. It is a white crystalline substance and is the lightest of all solid compounds. LiH is an ionic compound, Li^+H^-. It is decomposed with water to evolve hydrogen and is a ready source of the gas :

$$LiH + H_2O = LiOH + H_2$$

4.5 lbs. of LiH will furnish as much H_2 as contained in a steel cylinder of 200 cubic feet capacity when charged under 120 atmospheres. It is used for removing oxide scale from steel and as hydrogenating agent.

Lithium-aluminium hydride, $LiAlH_4$: This is obtained when anhydrous $AlCl_3$ is added to LiH in ether :

$$4\ LiH + AlCl_3 \xrightarrow{\text{ether}} LiAlH_4 + LiCl$$

$LiAlH_4$ is readily decomposed by water :

$$LiAlH_4 + 4H_2O \rightarrow LiOH + Al(OH)_3 + 4H_2$$

$LiAlH_4$ is a strong reducing agent and is used in organic chemistry with great advantages. $LiBH_4$ also has similar properties. Although $LiAlH_4$ is soluble in organic solvents, it is regarded as composed of Li^+ and AlH_4^- ions. AlH_4^- ion has tetrahedral structure.

The Anomaly of Lithium

The alkali metals as a group have a remarkable similarity in their chemistry but it is noticed that Li has certain unique physical and chemical properties different from other alkali metals. It is harder and has a higher melting point. It forms peroxide with great difficulty and reacts with nitrogen readily. The fluorides, carbonates and phosphates of lithium are insoluble in water as is the

case with the corresponding compounds of magnesium in group II. The organic derivatives of lithium are almost covalent.

The anomaly in the properties of Li is in accordance with the diagonal relationship in the Periodic Table of elements as discussed in Chapter 4.

As mentioned earlier, the relationship is due to the charge and the size of the elements and their ions. Li atom is the smallest of all the alkali metals and has only 2 electrons in the penultimate energy level, whereas all other alkali metals have 8 electrons. The ionic radii of Li^+ and Mg^{+2} are quite nearly the same (0.65—0.60Å). The ionic size is an important factor in determining the behaviour of elements in some aspects, and it is for this reason that Li and Mg have some similar properties.

Compounds of Sodium

Some of the important compounds of sodium are described here.

Sodium peroxide, Na_2O_2 : This is manufactured by passing small pieces of Na in aluminium trays through a furnace at 300°C while a current of dry and CO_2-free air is moving in the opposite direction. This is an application of the "counter current principle" and is widely used in industrial processes. The sodium metal moves in one direction while the air moves in the opposite direction.

Sodium peroxide is a yellow powder and absorbs moisture and CO_2 from atmosphere forming NaOH and Na_2CO_3. It evolves oxygen on strong heating. Oxygen can be readily prepared from Na_2O_2 by the action of hot water.

$$Na_2O_2 + 2H_2O = 4NaOH + O_2$$

Dilute acids in the cold liberate hydrogen peroxide but on heating with acids oxygen is evolved :

$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2 \text{ (cold and dilute)}$$

$$2Na_2O_2 + 2H_2SO_4 = 2Na_2SO_4 + 2H_2O + O_2 \text{ (heating)}$$

Carbondioxide also decomposes Na_2O_2 evolving O_2. This has been used for purifying air in closed spaces, such as submarines.

Sodium peroxide is a powerful oxidising agent. For instance, it converts $Cr(OH)_2$ into Na_2CrO_4 and also chromite, $FeCr_2O_4$ into ferric oxide and sodium

chromate. Sulphur dioxide is converted into SO_3. When Na_2O_2 is treated with absolute alcohol at 0°C, it gives sodium hydrogen peroxide, NaO,OH :

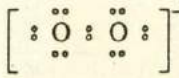
$$Na_2O_2 + EtOH = NaOEt + NaO,OH$$

Benzoyl peroxide is obtained by the action of Na_2O_2 on benzoyl chloride. This is a very good bleaching agent :

$$2C_6H_5COCl + Na_2O_2 = (C_6H_5CO)_2O_2 + 2NaCl$$

Na_2O_2 is used as an oxidising agent and as a bleaching agent. Na_2O_2 mixed with a little copper oxide is sold under the trade name "Oxone" for the preparation of oxygen. "Soda bleach", a mixture of Na_2O_2 and dilute HCl, is used for bleaching of fibres.

Sodium peroxide contains O_2^{-2} ions which consist of a chian of —O—O— in the molecular structure : Na—O—O—Na



Sodium hydroxide, NaOH : It is an important industrial chemical and is manufactured in large scale known as caustic soda. The principles of some of the methods are given below :

1. Causticisation of soda ash : Soda ash (Na_2CO_3) solution is heated with slaked lime, $Ca(OH)_2$, in calculated amount at a temperature of about 85°C, while steam is blown into the mixture. The process is known as "*causticisation*" or "*lime soda process*" :

$$Na_2CO_2 + Ca(OH)_2 = 2NaOH + CaCO_3$$

The precipitate of calcium carbonate is filtered off. The solution containing only 20% NaOH is evaporated to solid mass and then cast into sticks or cylinder.

2. The Löwig process : In this process a mixture of sodium carbonate and ferric oxide is strongly heated in a furnace to give sodium ferrite, $NaFeO_2$:

$$Na_2CO_3 + Fe_2O_3 = 2NaFeO_2 + CO_2$$

Sodium ferrite on treatment with hot water gives NaOH :

$$NaFeO_2 + 2H_2O = NaOH + Fe(OH)_3$$

3. The electrolytic method : A number of electrolytic cells have been developed for the production of caustic soda from NaCl solution. The principles of the method involved are : (i) electrolytic dissociation of NaCl, (ii) electrolysis of NaCl forming metallic sodium at the cathode and chlorine gas, Cl_2, at the anode, (iii) the instantaneous reaction of metallic sodium with water in the cell to give NaOH and H_2.

In the Castner-Kelner cell, mercury is used at the cathode in order to form sodium amalgam (Na–Hg) when metallic sodium is liberated. Sodium amalgam is unreactive towards strong brine. Sodium amalgam is made to react with water to form NaOH. The Castner-Kelner cell produces almost pure caustic soda :

$$Na\text{-}Hg + H_2O \rightarrow NaOH + H_2 + Hg$$

In the Solvay mercury cell which is a modification of Castner-Kelner cell, flowing mercury cathode is used. The sodium amalgam formed at the cathode is drawn out and is decomposed by water in a separated iron vessel. The solution of caustic soda is evaporated in iron pots to give solid product in the form of sticks or pellets. In all the cells, the graphite rods are used as anode because of evolution of Cl_2 gas from NaCl solution during electrolysis (Fig. 14—2).

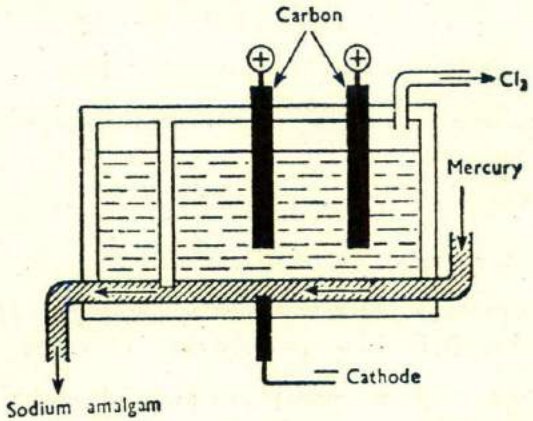


Fig. 14—2. Solvay's electrolytic cell for NaOH.

Properties : Caustic soda is a white crystalline solid, very hygroscopic and absorbs moisture and a little CO_2 forming a saturated solution. The solution slowly resolidifies by absorption of CO_2 when Na_2CO_3 is formed which is

sparingly soluble in NaOH solution. A strong solution of caustic soda is known as "*lye*" or "*soda lye*". NaOH is an ionic compound and melts and boils without decomposition. When dissolved in water, it evolves a great deal of heat due to the formation of a number of hydrates. NaOH liberates ammonia from ammonium salts and precipitates hydroxides from appropriate salt solution :

$$NH_4Cl + NaOH = NaCl + H_2O + NH_3$$

$$FeCl_3 + 3NaOH = Fe(OH)_3 + 3NaCl$$

Uses : Caustic soda is extensively used in the production of chemicals, rayons, soaps, textile, paper and pulp, dye stuff and petrolium refining. It is an item of the heavy chemical industries.

Sodium carbonate, Na_2CO_3 : It occurs in the natural salt deposit from dried-up lakes in many parts of the world. Na_2CO_3 is produced in commercial scale by several methods.

1. Le Blanch Process : This is an old method and Na_2CO_3 is produced by a series of chemical reactions. The starting materials are NaCl, H_2SO_4, $CaCO_3$ and coke. The following reactions take place :

$$NaCl + H_2SO_4 = NaHSO_4 + HCl\ (150°C)$$

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl\ (400°C)$$

Sodium sulphate is known as *salt-cake* and this is heated with coke and limestone, $CaCO_3$:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS$$

The solid mass (black ash) on lixiviation with water gives a solution of Na_2CO_3. Crude Na_2CO_3 is obtained on evaporating the solution.

2. Ammonia soda or Solvay process : Although both sodium carbonate, Na_2CO_3 and bicarbonate, $NaHCO_3$, can be made by the reaction of NaOH and CO_2 the use of NaOH is uneconomic :

$$NaOH + CO_2 = NaHCO_3$$

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$

The Solvay process is a model of economy in chemical industries and both Na_2CO_3 and $NaHCO_3$ are produced in very large scale, using brine and limestone as starting materials. Brine saturated with ammonia and carbondioxide, obtained from limestone or burning of natural gas, is passed through the carbonation tower :

$$CaCO_3 \xrightarrow{heat} CaO + CO_2$$

$$CO_2 + H_2O + NH_3 = NH_4HCO_3$$

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl$$

$NaHCO_3$ separates out as crystallie mass and NH_4Cl remains in solution. $NaHCO_3$ on heating gives Na_2CO_3 and CO_2 which is recycled to ammonical brine.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

The lime, CaO, formed during the roasting of $CaCO_3$, is added to NH_4Cl in solution to regenerate NH_3 gas and recycled to the brine :

$$CaO + 2NH_4Cl = CaCl_2 + H_2O + 2NH_3$$

In effect, the overall reaction in the Solvay process is,

$$2NaCl + CaCO_3 \rightleftharpoons CaCl_2 + Na_2CO_3$$

Due to extreme insolubility of $CaCO_3$, the reaction goes towards the left, but with the help of ammonia which is recovered, both $NaHCO_3$ and Na_2CO_3 are manufactured. An schematic representation of the process is given in Fig. 14—3.

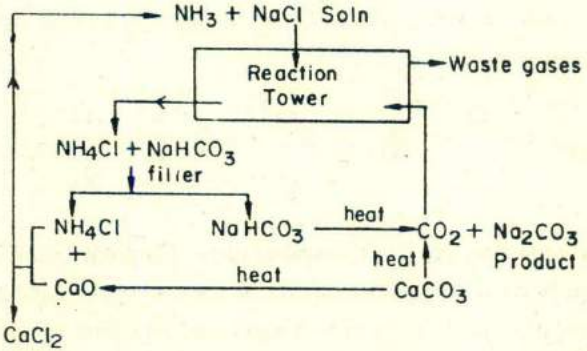


Fig. 14—3. Flow sheet of Solvay process for Na_2CO_3.

Since alkali carbonates are salts of strong bases and weak acid, they undergo extensive hydrolysis in H_2O forming MOH (M is an alkali metal) :

$$Na_2CO_3 + H_2O = NaOH + NaHCO_3$$

Na_2CO_3 crystallises with $10H_2O$ forming $Na_2CO_3.10H_2O$ (washing soda). But the vapour pressure of water at room temperature in equilibrium with $Na_2CO_3.10H_2O$ being greater than partial pressure of water in the atmosphere, it loses water when exposed to the air, a phenomenon known as *efflorescence*.

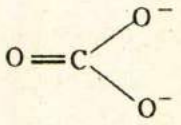
Na_2CO_3 is used in the manufacture of glass. Washing soda, $Na_2CO_3.10H_2O$, is used for laundering. Large amounts of Na_2CO_3 are used for making soap, paper and pulp, textiles and in petroleum refinery and water softening.

Baking soda, $NaHCO_3$, is used in baking powder and in alkali mixtures of doctors. In baking powder, $NaHCO_3$ liberates CO_2 either by heat or by reactions with $KHC_4H_4O_6$ (potassium hydrogen tartrate) etc. causing the dough to rise and give the desired lightness of bread.

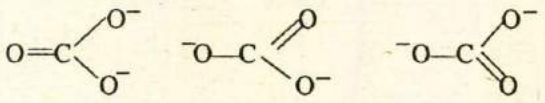
The CO_3^{-2} ion has the structure :



or



The arrangement is such that all the atoms in CO_3^{-2} lie in the same plane and all the O—C—O angles are equal (120°). Also all the three O—C bonds are equal. Thus each oxygen atom in CO_3^{-2} ion is identical in every respect, suggesting resonance structure :



Sodium chloride, NaCl (Common salt) : Sodium chloride is one of the most abundant and important minerals. Sea-water contains about 2.5 per cent of NaCl. There are vast deposits of rock salt in the Strassfurt region of Germany and in the U. S. A. During the dry season Rann of Ketch (India) has large areas

as bed of salt. The salt is obtained from underground deposits by mining and from sea-water by evaporation during the dry season in salt beds near sea coasts as in Chittagong district of Bangladesh. The salt obtained in this way is called *solar salt* and the mother liquor containing magnesium bromide is called *bittern*. NaCl obtained from sea-water or mines is impure.

Purification of NaCl : Salt is purified by dissolving it in water, concentrating the solution by evaporation and crystallising the salt. Impurities which are more soluble are retained in the solution. Salt obtained in this way is not very pure and contains, among others, $MgCl_2$ and $CaCl_2$, the presence of which makes the commercial salt moist during humid weather.

Pure NaCl is obtained by passing HCl gas to a saturated solution of the commercial salt. The solid NaCl is deposited in cubic crystals in the pure form due to common ion effect :

$$Na^+ + Cl^- + H^+ + Cl^- = NaCl \text{ (precipitate)} + HCl$$

Pure NaCl is generally called table salt. Sodium chloride is the usual source of a host of chemicals of great importance. Salt is the essential constituent of the foods of animals and human beings.

Sodium nitrate, $NaNO_3$: This is formed in nature by the interaction of organic matters with compounds of the soil. There are large deposits of $NaNO_3$ in Chile known as Chile Nitre or *"Caliche"*. Pure $NaNO_3$ is obtained from the *Chile Nitre* by lixiviating it with water, evaporating the solution and recrystallising. $NaNO_3$ is deliquescent whereas KNO_3 is not. KNO_3 is obtained from $NaNO_3$ by addition of KCl.

$$KCl + NaNO_3 = KNO_3 + NaCl$$

NaCl is removed as solid when the solution is evaporated. $NaNO_3$ is hygroscopic. $NaNO_3$ requires higher temperature (380°C) for decomposition to $NaNO_2$ and O_2 as compared to other nitrates.

Sodium nitrite, $NaNO_2$: Sodium nitrite is now-a-days an important commercial compound. This is obtained by various methods. For instance, N_2

and O_2 of air may be combined to form NO under electric spark and subsequently NO_2 is formed which dissolves in NaOH to give $NaNO_2$. This is also obtained when $NaNO_3$ is heated with Pb :

$$NaNO_3 + Pb = PbO + NaNO_2$$

$NaNO_2$ is extensively used for the manufacture of azo dyes and in organic synthesis. It has both oxidizing and reducing properties. It reduces $KMnO_4$ and liberates iodine from KI.

Sodium silicate, Na_2SiO_3 (Soluble glass or water glass) : This is obtained by melting together Na_2CO_3 and pure sand :

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

The product is a greenish blue glass. When this is heated with water under pressure, it slowly dissolves to give a thick heavy solution known as Water Glass. This is used as additive in soap, as a mordant, adhesive etc. $Na_2SiO_3.5H_2O$ crystals are readily soluble in cold water.

Sodamide, $NaNH_2$: When ammonia gas is passed over heated Na at about 300°C, $NaNH_2$ is produced :

$$2Na + 2NH_2 = 2NaNH_2 + H_2$$

$NaNH_2$ is decomposed by water to give NH_3 and with CO_2, forms cyanamide, $CNNH_2$:

$$NaNH_2 + H_2O = NaOH + NH_3$$
$$2NaNH_2 + 2CO_2 = Na_2CO_3 + H_2O + CNNH_2$$

Sodium azide is formed when $NaNH_2$ is heated with N_2O gas :

$$NaNH_2 + N_2O = NaN_3 + H_2O$$

Sodium azide is also obtained when liquid ammonia solution of $NaNO_3$ and $NaNH_2$ are warmed.

$$NaNO_3 + 3NaNH_2 = NaN_3 + 3NaOH + NH_2$$

All other alkali amides and azides are obtained in a similar manner.

Azidodithio carbonates are obtained when NaN_3 reacts with CS_2 in aqueous solutions :

$$NaN_3 + CS_2 = NaS.CSN_3$$

Sodium cyanide, NaCN : This is formed when $NaNH_2$ is heated with red-hot charcoal :

$$Na \xrightarrow{NH_3} \underset{\text{sodium amide}}{NaNH_2} \xrightarrow[\text{heat}]{+C} Na_2CN_2 \text{ (sodium cyanamide)}$$

$$\underset{\text{sodium amide}}{NaNH_2} + C \xrightarrow{\text{heat}} \underset{\text{(sodium cyanide)}}{NaCN}$$

NaCN is also obtained from coal gas which contains HCN and NH_3 :

$$HCN + NH_3 \xrightarrow[\text{Soln.}]{CuSO_4} (NH_4)_2Cu(CN)_3 \text{ (ammonium cuprocyanide)}$$

$$(NH_4)_2Cu(CN)_3 \xrightarrow{\text{dil } H_2SO} H_2O + NaCN \xleftarrow{NaOH} HCN\,(gas) + [CuCN + (NH_4)_2SO_4]$$

Sodium cyanide is used in electroplating and in the extraction of gold and silver. It is also used in organic synthesis and as a reducing agent.

Sodium sulphite, Na_2SO_3 : This is prepared from NaOH and SO_2 :

$$NaOH + SO_2 = NaHSO_3$$

$$2NaOH + SO_2 = Na_2SO_3 + H_2O$$

Both SO_2 and SO_3^{-2} ion are strong reducing agents. Na_2SO_3 is used in the manufacture of wood pulp. It is also used to remove excess chlorine in bleaching industry.

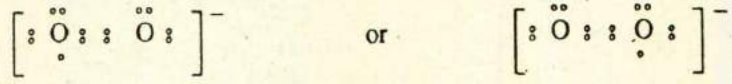
Compounds of Potassium

Most of the compounds of potassium are obtained in the like manner as described in the case of sodium. Only some of these which have properties peculiar to potassium will be described here.

Potassium oxides : K_2O, K_2O_2 and KO_2 are formed by direct union of K with oxygen at various conditions. Only the larger alkali metals K. Rb, give the superoxides, such as KO_2. The superoxides contain O_2^- ion as compared to the peroxides which has O_2^{-2} ions. Thus KO_2 is actually $K^+O_2^-$ and has crystal lattice similar to Na^+Cl^- in which Na is replaced by K^+ and Cl^- by O_2^-. KO_2 is decomposed in aqueous solution to give KOH and O_2 :

$$2KO_2 + 2H_2O = 2KOH + 2HO_2$$
$$\downarrow$$
$$H_2O_2 + O_2$$

Superoxide ion has the following structures :



Potassium hydroxide, KOH : Caustic potash is obtained in a similar manner as NaOH by electrolysis of KCl solution. It is used in the manufacture of soft soap and in organic reactions. Alcoholic caustic potash is used as a reagent. KOH is more soluble than NaOH.

Potassium chloride, KCl : This occurs in nature as *sylvine*. It is more soluble in water than NaCl, KCl is used in fertiliser.

Potassium bromide, KBr :This is obtained by the reaction of KOH and HBr :

$$KOH + HBr = KBr + H_2O$$

It is manufactured from iron bromide, a by-product of bromine manufacture :

$$FeBr_2.2FeBr_3 + 4K_2CO_3 \xrightarrow{4H_2O} Fe(OH)_2.2Fe(OH)_3 + 8KBr + 4CO_2$$
$$\downarrow \text{filtered and crystallised}$$
$$KBr$$

It is a white crystalline solid and is used in photography and in medicine as sedative.

Potassium iodide, KI : This is obtained in a similar manner as KBr. Iron iodide is first obtained by the reaction of iron filings and iodine :

$$Fe + I_2 \xrightarrow{H_2O} FeI_2.2FeI_3$$
$$\downarrow \text{boiled } K_2CO_3 + H_2O$$
$$KI$$

This is also obtained from KOH, I_2 and carbon :

$$6\,KOH + 3I_2 + 3C = 6KI + 3H_2O + 3\,CO$$

Potassium iodide is a white solid, dissolves in water and alcohol. It is a reducing agent. An oxidising agent liberates iodine from KI.

Potassium fluoride, KF : This is obtained by evaporating a neutral mixture of HF and KOH in a platinum dish. When the neutral mixture is treated with more HF and recrystallised, the product is potassium hydrogen fluoride, KHF_2, known as *Fremy's salt.*

Potassium cyanide, KCN : This is obtained from potassium ferrocyanide when it is heated strongly alone or with metallic potassium :

$$K_4Fe(CN)_6 = 4\,KCN + Fe + 2C + N_2$$

$$K_4Fe(CN)_6 + 2K = 6\,KCN + Fe$$

Potassium cyanide, KCN, is also formed when calcium cyanamide is heated with KCl and carbon in an electric furnace :

$$CaCN_2 + C + 2KCl = CaCl_2 + 2KCN$$

High temperature reaction between Na_2CO_3 or K_2CO_3, C and N_2 produces NaCN or KCN as the case may be :

$$Na_2CO_3 + 4C + N_2 = 3CO + 2NaCN$$

KCN is a deadly "poison" soluble in water and alcohols. It is used in the extraction of gold and as an analytical reagent. Cyanides are extremely important as a metal complexing agent. The extreme poisonous nature is due to complexing of metal atoms present in the enzyme of the animal system. Cyanide complexes are only slightly dissociated as in the case of $K_4Fe(CN)_6$ so that both Fe and CN^- cannot be detected. Cyanide ions stabilizes the various valence states of metal ions which are otherwise unstable in simple salts. For example, Mn^{+1}, Mn^{+3}, Ni^{+1}, Cu^{+1} etc. form stable compounds with CN^- ion.

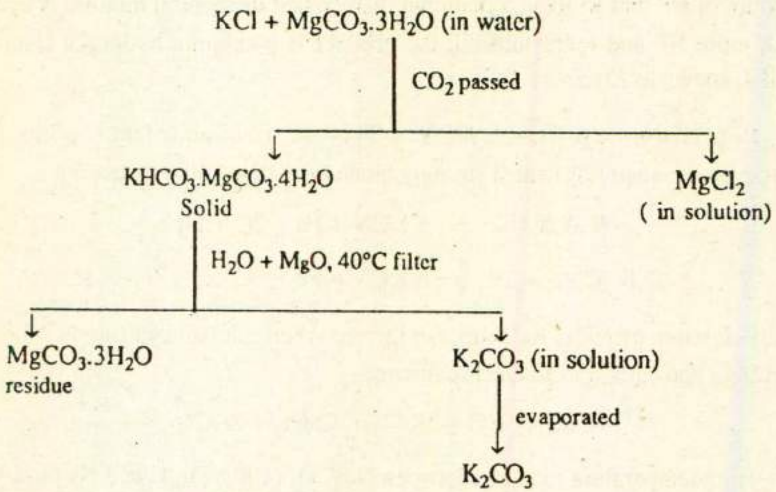
Potassium carbonate, K_2CO_3 : It is extracted from wood ash. It is obtained by the reaction if KCl with H_2SO_4 and then by heating the product with coke and limestone :

$$2KCl + H_2SO_4 = K_2SO_4 + 2HCl$$

$$K_2SO_4 + 2C = K_2S + 2CO_2$$

$$K_2S + CaCO_3 = K_2CO_3 + CaS$$

K_2CO_3 is now usually made by the reaction of KCl and $MgCO_3.3H_2O$ in presence of CO_2 :



K_2CO_3 is a very hygroscopic solid and is readily soluble in water forming a strong alkaline solution due to hydrolysis. When CO_2 is passed in a saturated solution of K_2CO_3, potassium bicarbonate, $KHCO_3$, is formed :

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_2$$

Potassium bicarbonate, $KHCO_3$, is much more soluble than $NaHCO_3$ and hence cannot be made by Solvay's process since crystals of $KHCO_3$ are not deposited. K_2CO_3 is easily fusible and is used as fusion mixture with Na_2CO_3.

Rubidium and cesium compounds : These are rare metals and occur in minerals from which these compounds are isolated for chemical investigations and research. Cs is the most electropositive of all elements and CsOH is the strongest base obtained by double decomposition between cesium sulphate and barium hydroxide. Rubidium hydroxide, RbOH, is similarly prepared. Rubidium and cesium salts are more soluble than the corresponding potassium salts. They easily form superoxides, RbO_2 and CO_2 besides other oxides.

Spectra of Alkali Metals and Their Compounds

When salts of the alkali metals are heated at a moderate temperature, as in the Bunsen Flame, characteristic colours are produced. These colours serve as a means for identification of the alkali metals. The emission of visible light is due to the low value of the ionization constant. The following flame colourations are produced :—

Li—Brilliant crimson
Na—Golden yellow
K—Violet (Lavender)
Rb—Lilac red
Cs—Bright blue,

QUESTIONS AND PROBLEMS

1. Give a brief account of the properties of the alkali metals, emphasizing the gradation of properties with increasing atomic number. How would you explain these properties on the basis of the atomic structure of the alkali metals ?
2. Describe preparation, properties and some of the uses of sodium bicarbonate.
3. Explain why alkali metals are highly reactive elements,
4. (a) Discuss briefly the general chemistry of the alkali metals with special reference to the gradation of the properties with increasing atomic number. (b) Discuss the anomalies in the chemistry of lithium and compare it with that of magnesium.
5. Describe the preparation, properties and uses of sodium cyanide.
6. Outline, with the help of a diagram, the manufacture of washing soda from sodium chloride by the Solvay process. Explain the chemistry of this process, drawing attention to physio-chemical principles involved.
7. Discuss the properties of lithium with special reference to its position in the Periodic Table. Compare and contrast its properties with those of sodium.
8. Explain :—
   (a) Why metallic sodium does not occur free in nature ?
   (b) Why is sodium carbonate or calcium chloride added to the electrolyte in the electrolysis of sodium chloride ?

(c) How will you prove that NaH contains the negative hydride ion ?

(d) Why are alkali metals electropositive ?

9. Outline the chemistry of the Solvay process for the production of sodium carbonate. Can you manufacture $KHCO_3$ by the Solvay process ?

10. Discuss the relative stabilities of alkali metal carbonates.

11. Explain the apparent anomalous properties of lithium in relation to other alkali metals.

12. Explain the reducing actions of alkali metals.

13. Give the method of preparation of lithium aluminium hydride.

14. Explain why alkali metals are highly reactive.

15. Write note on preparation, properties and uses of $NaHCO_3$.

16. Of the alkali metals, which has the lowest ionization potential and greatest oxidation potential.

17. Which alkali metal forms the most highly ionic compound ?

18. Which alkali metals form superoxides when burnt in air ?

19. What would happen if you keep sodium metal immerged in kerosene, ethanol, linseed oil and water ?

20. Alloys of lithium and sodium are used as heat transfer media in nuclear reactors. Explain.

21. Explain why Li is a better reducing agent than Cs.

CHAPTER 15

THE COINAGE METALS

(Elements of Group IB)

Copper, silver and gold are elements of sub-group **IB** in the Periodic Table. They occur in nature in the free state and are also easily extracted from their minerals. For this reason, they are known from ancient time and have been used for the purpose of making coins and are, therefore, known as the *coinage metals*. Because of their stability and non-reactive nature, particularly of silver and gold, they are also known as noble metals which include **Ir** and **Pt** also. These metals can withstand wear and exposure to the air and moisture and maintain their lustre without tarnishing. The single electron in the outermost orbital of the coinage metals is very firmly held by the positive nucleus.

The Electronic Structure

The metals of group **IB** follow a completely filled **d** level of transition elements. They have a single **s** electron in their outermost level and are, therefore, expected to show similar properties as the alkali metals, i.e. group **IA**. The electronic structures of the coinage metals may be written as follows :

Cu (29)—$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$ (Ar core, $3d^{10}\ 4s^1$)

Ag(47)—$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^1$ (Kr core, $4d^{10}\ 5s^1$)

Au(79)—$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14} 5s^2\ 5p^6\ 5d^{10}\ 6s^1$

(Xe core, $4f^{14}\ 5d^{10}\ 6s^1$)

The chemistry of copper, silver and gold is dependent upon the outermost s^1 electron and also the adjacent **d** electron which is different from that of the group **IA** metals. These metals, therefore, show characteristics of the transition elements.

Physical properties : Some of the physical properties of copper, silver and gold are listed in Table 15·1.

Table 15·1. Physical properties of copper, silver and gold.

Properties	*Cu*	*Ag*	*Au*
At. No.	29	47	79
At. Wt.	63.57	107.88	197.2
Outer electron orbitals	$3d^{10}4s^1$	$4d^{10}5s^1$	$5d^{10}6s^1$
Colour of metal	Red	Shining white	Yellow
Atomic radius (Å)	1.28	1.44	1.44
Ionic radius (Å)	Cu^+ 0.96 Cu^{+2} 0.69	Ag^+ 1.26	Au^+ 1·37
Ionization potential (ev)	7.71	7.54	9.18
Oxidation states	+1, +2	+1	+1,+3
Density at 20°C (g/cm^3)	8.92	10.5	19.3
Melting point (°C)	1083	960	1063
Boiling point (°C)	2310	1950	2600
Electronegativity	1.75	1.42	1.42
Oxidation potential	−0.52	−0.8	−1.68
$M = M^+(aq.) + e^-$ Standard electrode potential (v)	Cu/Cu^{+2}–0.34	Ag/Ag^+ –0.8	Au/Au^{+3}–1.5

It is interesting to note that copper and gold are coloured metals whereas silver is white. Whenever we find a colour in a chemical substance it is due to the excitation of low-lying energy level produced by a low-energy photon of visible light corresponding to an energy of about 1 to 3 ev. If we examine the electronic structures of copper, silver and gold, we find that all the three metals undergo the transition $d^{10} \rightarrow d^9s^1$. The energy needed for this transition is 2·7 ev for copper, 4·8 ev for silver, and 1·9 ev for gold. Thus copper and gold absorb visible light and are coloured. Whereas silver absorbs in the invisible ultraviolet and, hence, is a white silvery metal. The variable oxidation states of the coinage metals is also due to the presence of d electrons which undergo transition.

The gradation in the physical properties is not very well-marked in many cases. Copper, silver and gold have melting points near about 1000°C. The

atomic radii of Ag and Au are almost the same due to the lanthanide contraction. The ionization potentials for removing the s^1 electron are near about the same but it is easy to remove electrons from the inner 2—6—10 core and requires less energy. Moreover, the d electrons participate in covalent bonding. Thus, we have Cu^{+2} and Au^{+3}, very common ions.

The values of oxidation-reduction potential provide a clue to the inertness of the elements of group IB in the metallic state as compared with that of alkali metals which have much greater values. The resistance to oxidation as expressed in terms of the values of oxidation potential results from the following factors or a combination of these :—

(i) High heat of sublimation to the atoms.

(ii) High ionization potential.

(iii) Low energy of hydration for the positive ion.

In the coinage metals the s^1 electron (valence electron) is incompletely shielded by the inner d orbitals. Hence the ionization potentials for these metals are high. Due to incomplete shielding, the nuclear charge of the adjacent atoms are appreciably attracted by the neighbouring electron clouds and the break-up of the metallic structure to isolated atoms of the metals is extremely difficult resulting in greater heat of sublimation. Although the hydration energies of the coinage metals are high and they are expected to undergo easy oxidation, their effects are reduced to a great extent by the high sublimation energies and high ionization potentials.

Although the fairly high ionization potential would not suggest high electrical conductivity, Cu, Ag and Au are fairly good conductors of electricity because of the unpaired valence electron.

Chemical properties :

An idea of the chemical properties can be had from the electronic structures and the physical constants discussed before. The variable oxidation states and stable oxidation states do not follow any set pattern, although all the three metals can have oxidation states, +1, +2 and +3. Cu is more stable in +2 state, Ag in +1 state and Au in +3 state.

The reactions of various agents are given below :—

(a) Action of air : The oxygen of the air combines only with Cu on heating forming Cu_2O and CuO. Ag and Au do not combine with oxygen at all. Ag becomes tarnished in air on long exposure due to the presence of other gases, such as H_2S, SO_2, CO_2 etc. In pure dry air, Cu remains bright, but the surface of Cu becomes covered with green film of basic sulphate, $CuSO_4$, $3Cu(OH)_2$, in humid air containing SO_2 wrongly attributed to basic carbonate, although occasionally some basic carbonates are formed in presence of CO_2.

(b) Action of water : Water has practically no action on these metals at ordinary temperature.

(c) Reaction of acids : Dilute HCl has also no action on Cu, Ag and Au. Copper readily dissolves in dilute nitric acid with the evolution of nitric oxide :

$$3Cu + 8HNO_2\,(dil.) = 4H_2O + 2NO + 3Cu(NO_3)_2$$

Copper dissolves slowly in hot concentrated HCl with evolution of hydrogen but more rapidly in hot conc HBr and HI forming cuprous compounds. Ag is dissolved in hot dil HNO_3 and in hot conc. HI with evolution of hydrogen. Silver is also attacked by boiling conc. H_2SO_4 as in copper :

$$2Cu + 2HI = Cu_2I_2 + H_2$$

$$Ag + 2HNO_3 = AgNO_3 + H_2O + NO_2$$

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$$

Gold is not attacked by any single acid except selenic and iodic acid. It is dissolved by chlorine water or by aqua regia which is a mixture of HNO_3 and HCl.

(d) Reaction of alkali : Even a strong alkali has practically no action on these metals. Silver and gold resist action of alkalies even in the fused states and hence are used for crucibles for fusion with caustic alkalies. Aqueous ammonia in the presence of air dissolves copper and gives a blue solution containing $Cu(NH_3)_4^{+2}$ ion.

(e) Reaction of hydrogen : Copper, silver and gold do not react with hydrogen directly. However, CuH and AgH have been reported to be formed but appear to be doubtful.

*(f) **Reaction of halogen*** : Cuprous halides of the general formula CuX, are formed with all the halogens. Similarly, Ag gives AgX but also forms Ag_2F with flourine. With chlorine and bromine gold forms $AuCl_2$ and $AuBr_3$. AgF_2 is formed by the action of fluorine on silver powder.

*(g) **Reaction of sulphur*** : Cu_2S is one of the main ores of copper. It is also formed when Cu is heated in excess of sulphur :

$$2Cu + S = Cu_2S$$

Cupric sulphide, CuS, is not formed because it is decomposed to cuprous sulphide, Cu_2S, at 300°C :

$$2\,CuS = Cu_2S + S$$

Comparison of the Alkali Metals and the Coinage Metals

Because of the fact that alkali metals of group IA and the coinage metals of group IB each has one unpaired electron, s^1, in the outermost level, the elements of these two groups might be expected to behave in a similar manner. The elements in both groups are good conductors of electricity and show oxidation state of +1. The univalent compounds are formed with analogous formulas and posses similar crystal structures. For instance.

Na_2O	Ag_2O
NaCl	AgCl
Na_2SO_4	Ag_2SO_4
$K_2SO_4,Al_2(SO_4)_3,24H_2O$	$Ag_2SO_4,Al_2(SO_4)_3,24H_2O$

But the similarities do not extend beyond this and there are a great deal of dissimilarities both in physical and in chemical properties of the elements of the two sub-groups. The dissimilarities in the properties of alkali metals and coinage metals are due to the fact that the outermost s^1 electron in the alkali metals is situated after an inert gas s^2p^6 electrons whereas in the coinage metals the outermost s^1 electron comes after the d^{10} electrons. The dissimilarities are listed below.

(1) Electronic structures are different although they have s^1 electron in the outermost level.

Z		*Alkali metal*		Z		*Coinage metal*	
3	Li	(2),	$2s^1$	29	Cu	(18),	$3d^{10}4s^1$
11	Na	(10),	$3s^1$	47	Ag	(36),	$4d^{10}5s^1$
19	K	(18),	$4s^1$	79	Au	(68),	$5d^{10}6s^1$
37	Rb	(36),	$5s^1$				
55	Cs	(54),	$6s^1$				
87	Fr	(86),	$7s^1$				

(2) The alkali metals are most reactive elements while the coinage metals are unreactive and difficult to oxidise.

(3) The alkali metals never occur in nature in free state, but always in combination, whereas the coinage metals are found abundantly in free state.

(4) The alkali metals have only one oxidation state, +1, whereas the coinage metals may lose one or more than one electron per atom to give +1, + 2 and + 3 oxidation states particularly in gold.

(5) The alkali metals have melting points ranging from 180°C for lithium to 28·4°C for cesium. The coinage metals have melting points near about 1000°C.

(6) The alkali metals form strong bases because of their small charge (+) and large sizes. Their hydroxides are strongly ionized and their halides are not hydrolysed. The coinage metals do not give strongly basic oxides or hydroxides. Silver oxides when moist is only feebly basic and $Au(OH)_3$ is amphoteric.

(7) The coinage metals can be worked and used as metals because these are heavy, ductile and malleable. The alkali metals cannot be handled easily and are kept in kerosene.

(8) The alkali metals are never found in anions and practically have no complex cations. The coinage metals form large number of stable complexes, both as cations and anions, such as,

$K[Ag(CN)_2]$, , $KAuO_2$

$[Ag(NH_3)_2]Cl$, $[Cu(NH_3)_4](NO_3)_2$

$K[Au(CN)_2]$, $[Cu(NH_3)_4]Cl$, $K_2[Cu(CN)_4]$

(9) Most compounds of the alkali metals are soluble in water ; this is not the case with the coinage metal compounds. Oxides, sulphides and chlorides of the alkali metals are soluble in water while the corresponding salts of Cu, Ag and Au are insoluble (excepting $AuCl_3$ and $CuCl_2$).

(10) Many of the ions and compounds of the coinage metals are coloured, whereas those of the alkali metals are colourless. The alkali metals form coloured compounds only when the anions are coloured as in $K_2Cr_2O_7$, $KMnO_4$ etc.

(11) The alkali metals are of recent discovery and their uses are only scientific and technological. The coinage metals were among the first to be used by primitive men from time immemorial for ornaments and for coinage purposes.

Extraction of Coinage Metals

Extraction of copper : Copper is generally extracted from its ores.

Ores of copper : The important ores of copper are,

Copper pyrite—	$CuFeS_2$ or Cu_2S, Fe_2S_3
Chalcocite (copper glance)—	Cu_2S
Malachite—	$CuCO_3$, $Cu(OH)_2$
Cuprite—	Cu_2O

The principle of extraction : The metallurgical operation involving the extraction of copper from its ores is of technological importance. Since the most important ores contain also iron and sulphur, any procedure for extracting pure copper from such an ore require a number of operations. Both dry and wet methods are used for the extraction of copper which is purified by electrolytic method.

Large amount of copper is obtained from copper pyrites, $CuFeS_2$, by smelting. The separation of Fe and S from Cu is the main task and is difficult since bonds between Cu and S are stronger than those between Fe and S. But Fe is removed by oxidation as ferrous silicate which dissolves in the slag leaving Cu_2S. Partial roasting of Cu_2S in air converts it to Cu_2O which reacts with Cu_2S to form metallic copper. The reactions involved are,

$$2CuFeS_2 + 4O_2 = Cu_2S + 2FeO + 3SO_2$$

$$FeO + SiO_2 = FeSiO_3$$

$$Fe_2O_3 + 3SiO_2 = Fe_2(SiO_3)_3$$

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$

$$Cu_2S + 2CuO = 4Cu + SO_2$$

The process of extraction from the copper pyrites.

(1) Concentration of the ore : Copper pyrite ore is first concentrated by froth floatation process.

(2) Roasting : The concentrated ore is then roasted in furnace. This drives off moisture, removes part of sulphur as sulphur dioxide and also arsenic and antimony are removed. The roasted ore is called "calcine" which consists of Cu_2S, FeS, FeO and SiO_2.

$$2CuFeS_2 + O_2 = Cu_2S + 2FeS + SO_2$$

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$

$$2FeS + 3O_2 = 2FeO + 2SO_2$$

(3) Smelting : The roasted ore is smelted in a blast furnace with limestone and sand for the formation of slag. Limestone serves as a flux :

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2$$

$$FeO + SiO_2 = FeSiO_3$$

The impure Cu_2S containing FeS obtained after smelting is called "matte".

(4) Bessemerisation : The matte is reduced in a Bessemer convertor by blowing air through the molten material. The air first oxidises FeS to FeO and SO_2. Sand is added to form a slag of $FeSiO_3$. The air blast converts some Cu_2S to Cu_2O which instantaneously reacts with Cu_2S to give metallic copper :

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S = 6Cu + SO_2$$

Some CuO is also produced by the air blast. This is removed by stirring the metal with poles of green wood, the resulting gases acting as reducing agent. The copper obtained has a characteristic appearance and is called "blister copper".

Refining of blister copper: The impure copper is cast into large plates which are used as anodes in the electrolytic purification of copper. Thin sheets of pure copper serve as the cathodes and $CuSO_4$ solution acidified with H_2SO_4 serves as the electrolyte. A schematic diagram of the electrolytic cell is given in Fig. 15—1. The impure copper passes into solution from the anodes

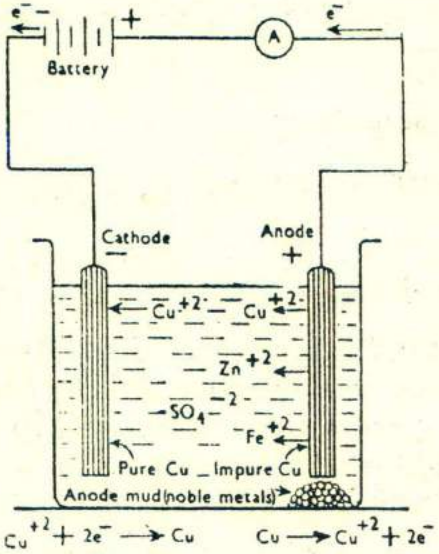
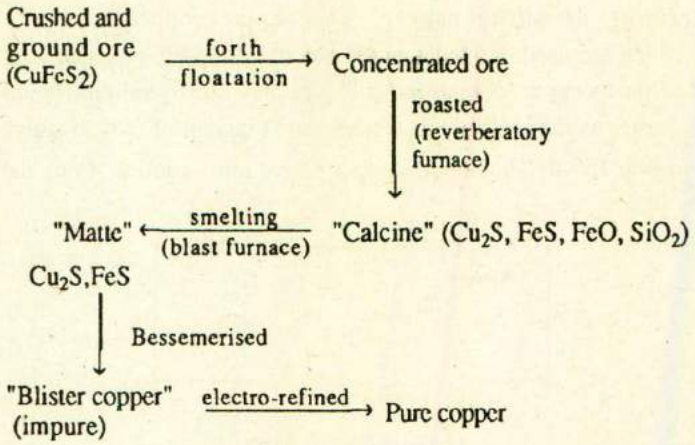


Fig. 15—1. Refining of copper by electrolytic method

and pure copper is deposited on the cathodes as the electrolysis proceeds. The principal impurities are silver and iron. The voltage applied to the electrolytic cell is just kept below the voltage necessary for silver deposition. Silver does not go into solution but along with gold it falls to the bottom as "anode mud" which also contains bits of slag and Cu_2O. Silver, gold and platinum group metals are recovered from the anode mud as valuable by-products. Fe and Zn pass into solution and are not deposited. The copper deposited is in extremely pure form when the voltage is controlled at precisely the right value. The cost of electro-refining of copper is generally met from the precious metals recovered from the "anode mud."

The entire process for the extraction of copper may be given schematically as :



Hydrometallurgy of Copper

In this process Cu_2S,FeS_2 is converted to $CuSO_4$. This is based on the fact that CuS or Cu_2S is more easily oxidized to $CuSO_4$ than FeS or Fe_2S_3. The ore is exposed to the weathering action of air and rain for a long time. Copper sulphate and iron sulphate are formed which are leached by water. Metallic copper is then precipitated by adding iron filings.

In order to hasten the conversion of the ore to $CuSO_4$ and $FeSO_4$, the ore is first roasted at a controlled temperature in a reverberatory furnace. Both $CuSO_4$ and $FeSO_4$ are formed. Some of the $FeSO_4$ is converted to Fe_2O_3, but $CuSO_4$ remains unaffected because it requires higher temperature to decompose to CuO. Even if some CuO is formed it is converted to $CuSO_4$ by SO_2 gas liberated during roasting. Copper sulphate is leached with water along with some $FeSO_4$. Copper is precipitated from the solution by adding scraps of iron or by electrolytic process :

$$CuFeS_2 + O_2 \longrightarrow CuSO_4 + FeSO_4 + SO_2$$

$$FeSO_4 + O_2 \longrightarrow Fe_2O_3 + SO_2$$

$$CuO + SO_2 \longrightarrow CuSO_4$$

$$CuSO_4 + Fe \longrightarrow Cu + FeSO_4$$

Extraction of Silver

Ores of silver : Almost pure silver is found in nature mixed with copper and gold. Important ores of silver are :

Argentite (silver glance)—Ag_2S

Haloargyrite—AgCl, AgBr, AgI

(AgCl is also known as horn-blende)

Pyroargyrite—Ag_5SbS_4

Some silver is found in galena, PbS.

A large part of silver produced in the world comes from the residues (anode mud) obtained from the electrolytic refining of copper.

The extraction of silver is carried out by various techniques. The principles of these techniques are described here.

1. The cupellation process : When silver and lead ores are smelted together, they form an alloy of lead and silver which on heating forms lead monoxide, PbO, and metallic silver. The lead monoxide forms a scum on the surface and is blown off giving the metallic silver. The alloy is heated on a 'cupel' or oval-shaped wrought-iron vessel filled with bone-ash and hence the process is known as *cupellation process*.

2. The amalgamation process : This process has become now almost out of use. This is based upon the fact that silver ores mixed with some salt and roasted pyrites and ground to a mud with water form silver chloride, AgCl. When mercury is thoroughly mixed with the slime, AgCl reacts with mercury to produce silver. The liberated silver forms amalgam with excess of mercury. The amalgam on distillation gives metallic silver while mercury is distilled off :

$$2Cu_2Cl_2 + Ag_2S \rightarrow Cu_2S + 2AgCl \qquad 2AgCl + 2Hg = 2Ag + Hg_2Cl_2$$

3. The Parke's process : This is based upon the fact that molten lead dissolves about 1% of zinc and molten zinc about 1% of lead. But silver is completely soluble in molten zinc. Hence, when molten zinc is added to fused lead-silver alloy. silver goes into solution in zinc forming zinc-silver alloy which solidifies and floats on the surface of molten lead. The process is called desilverisation of lead and depends upon the parting of silver from lead to zinc.

Silver can be obtained from zinc-silver alloy by distillation when zinc is distilled off.

4. The cyanide process: Most of the silver is now obtained by the cyanide process. This is dependent upon the formation of the complex dicyanoargentate ion, $Ag(CN)_2^-$, with cyanide, CN^- ion. Silver metal and all its compounds are easily soluble in alkali cyanides in presence of air. The hydrometallurgy of silver is based upon the fact that the metallic silver is deposited from the cyanide solution upon the addition of zinc or aluminium. The air blast serves to stir up the solution and brings about the oxidation of the sulphide present in Ag_2S.

$$4Ag + 8NaCN + 2H_2O + O_2 = 4NaAg(CN)_2 + 4NaOH$$

$$Ag_2S + 4NaCN = 2NaAg(CN)_2 + Na_2S$$

The sodium sulphide is oxidised to sulphate in presence of air :

$$4Na_2S + 2H_2O + 5O_2 = 2Na_2SO_4 + 4NaOH + 2S$$

The silver is deposited from the solution by zinc :

$$2NaAg(CN)_2 + Zn = 2Ag + Na_2Zn(CN)_4$$

The process of extraction of silver may be given schematically as :

Grinded ore of Ag (Ag_2S) $\xrightarrow[\text{floatation}]{\text{forth}}$ Concentrated ore

$\downarrow$ dil. NaCN soln.

$NaAg(CN)_2$ solution $\xleftarrow[\text{blown}]{\text{air}}$ Suspension

filtered & $\downarrow$ Zn added

Precipitated Ag $\xrightarrow[\text{dried \& fused}]{\text{filtered,}}$ Metallic silver

Purification of silver : Silver is refined by electrolysis of silver nitrate solution in presence of about 1% HNO_3. The cathode is a thin plate of silver and the impure blocks of silver serve as anode. Silver is deposited on thin silver

cathode, copper dissolves and gold collects as a mud. The process is also known as parting of silver from gold.

Extraction of Gold

Sources of gold: (1) Gold is found chiefly in the form of metal. The nuggets of gold are found scattered through gravel and in small particles in the veins of rocks or sands. Alluvial sands of river beds contain some gold particles in certain places. (2) In the combined state it is found as gold telluride, $AuTe_2$, and double telluride, $AuAgTe_4$, known as silvanite. (3) Au is obtained as a by-product from the extraction of Ni, Cu and Ag by the process of electrometallurgy.

Metallurgy of Gold

(1) Process depending on the specific gravity of gold : From ancient times gold has been obtained by several physical processes, such as "panning", "sluicing" etc. In these methods gold-bearing sands and gravels are washed with water to separate the lighter particles from the heavy particles of gold.

Hydraulic mining of gold has been developed to separate gold from rocks with powerful streams of water. The gold is washed into sluices which are long troughs and deposited free from sand and clay.

(2) Process depending on the amalgamation with mercury : Amalgamation process has also been in use. Finely powdered rocks are washed over plates of copper coated with mercury. Gold contained in the slime dissolve in the mercury. The gold amalgam is removed and distilled. Mercury is distilled off and the gold residues known as "taillings" are refined.

(3) The cyanide process : The process of extraction of gold by cyanide process is based on the same principle as described in the case of silver. In fact, the two metals are extracted simultaneously. The gold-bearing rocks are first crushed and pulverised in stamp mills. The pulverised ore is washed with water and treated with a dilute solution of NaCN through which air is blown. In presence of air (oxygen) gold dissolves in a solution of NaCN or KCN when finely powdered ore is treated with the reagent :

$$4Au + 8KCN + 2H_2O + O_2 = 4KAu(CN)_2 + 4KOH$$

The gold is precipitated from the solution by displacement reaction with Zn or Al :

$$Zn + 2KAu(CN)_2 = 2Au + K_2Zn(CN)_4$$

Refining of gold : Gold obtained by any of the process is impure and contains silver and also lead, copper, zinc etc. The refining or 'parting' of gold is done by—(i) electrolysis or (ii) by dissolving the impurities in a chemical reagent.

(i) The impure gold is made the anode and a thin sheet of pure gold is the cathode. The electrolytic solution is chlorauric acid. The gold deposits on the cathode and silver is precipitated as silver chloride, AgCl.

(ii) The chemical process of the parting of gold is based on the treatment of impure gold with nitric acid or sulphuric acid in which silver dissolves and gold remains unaffected.

Uses of Coinage Metals

Uses of copper : Copper is second in importance to iron because of its wide range of uses.

The most important use of copper is in the production of electrical wiring.

It is also used for making utensils in the fermentation industries and for making coins. Since copper is electrically deposited in thin sheets which are smooth and tough, it is used in electrotyping for printing books and integrated circuits in electronics.

A large number of useful alloys of copper are made. Some of the important alloys of copper are :

(i) ***Brass*** : Cu : 60—80% and Zn : 20—40%. It has yellow colour and can be made into any desired shape.

(ii) ***German silver*** : Cu : 50—60% : Zn : 20%; Ni : 20—25%. It is white in colour and largely used in making utensils and table wares and also ornaments.

(iii) ***Bronze*** : Cu : 70—95% ; Zn : 1—25% ; Sn : 1—18%. It is a tough alloy and is used in making machinery parts and propellers.

*(iv) **Phosphor bronze*** : Bronze containing P—1% is hard, elastic and tough.

*(v) **Monel metal*** : Cu—30% ; Ni—67% and Fe or Mn—3%. This alloy is resistant to chemical action and has great strength. It is used in chemical industries.

*(vi) **Nickel coin*** : Cu—75%. Ni—25%. It is used for making coins.

Uses of silver : Silver is largely used for making coins, silver wares and ornaments. Silver is too soft and is, therefore, hardened by alloying with copper and other metals. Silver is also used in making dental alloys and mirrors. Silver salts are used in photography.

Recently silver alloys have been used as bearing metals in automobiles, aeroplanes and locomotives. High grade stainless steel containing about 0.3% silver has been made.

Uses of gold : Gold is a precious metal and has a permanent bright lustre. It is used in making ornaments and jewellery.

The unit of fineness of gold : Pure gold is a soft metal and it is generally alloyed with copper to make it hard. The fineness of gold is expressed in *carats*. Pure gold is 24 carats.

Gold is used for gold plating and gilding.

Colloidal gold is made by reducing gold chloride solution with hydrazine etc.

Purple of Cassius : This is a combination of gold with colloidal stannic acid. This is used as pigment in making red glass and high class pottery. This is made by mixing gold chloride with stannous chloride solution.

Compounds of Coinage Metals

Some important and well-known compounds of copper, silver and gold are described here.

Compounds of copper : Copper forms two series of compounds having copper atoms in two oxidation states of + 1 and + 2. This can be easily visualized from the electronic structures of Cu, Cu^{+1} and Cu^{+2} states :

$Cu\ (29) \quad -1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

$Cu^+ \quad -1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

$Cu^{+2} \quad -1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

Thus when one electron in the outermost level of the copper atom is used in bond formation, we get cuprous compounds. With two electrons removed, one from 4s and another from 3d level, we get cupric compounds.

There are marked differences in the stabilities of cuprous and cupric compounds. Binary compounds of cuprous Cu(1), are quite stable, such as halides, oxides, but the oxyacid salts of Cu^{+1} are readily decomposed by water. Cu^{+2} forms quite stable oxycompounds while its binary salts are unstable and are decomposed spontaneously. $CuSO_4$ is stable whereas CuI_2 is not. The electronegative character of the anions has a bearing on the properties of Cu^{+1} and Cu^{+2} compounds since the power to draw electrons from the 4s and 3d levels are involved. Thus in water Cu^{+1} ion normally undergoes disproportionation reaction giving Cu^{+2} ion and metallic Cu :

$$2Cu^+ \longrightarrow Cu^{+2} + Cu(solid)$$

The stable compounds of Cu^{+1} are insoluble in water, such as CuI, CuCl, CuBr, CuSCN. These are generally white and the chemistry of Cu^{+1} thus resembles that of Ag^{+1} in this respect.

However, unstable Cu^{+1} and Cu^{+2} compounds are made stable by complexing agents. Thus stable Cu^{+2} compounds, such as,

$[Cu(NH_3)_4]I_2$ or $[Cu(NH_2—CH_2—CH_2—NH_2)_2]I_2$

exist and are soluble in water. Even the oxyacid anions of cuprous salts which do not exist as such in water have been made stable by complexing agents. Thus cuprous nitrate,. $CuNO_3$, is stabilized by complexing with thiourea and ethylene thiourea giving

$[Cu\ (ethylene\ thiourea)_4]NO_3$ or $[Cu(etu)_4]_2SO_4$

Monovalent copper forms complexes with NH_3, $Cu(NH_3)_2^+$ and also with halides CuX_2^-. KCN gives complexes $KCu(CN)_2$ and $K_3Cu(CN)_4$. Cu^{+1} complexes are generally colourless in contrast to Cu^{+2} complexes which are intensely coloured.

Compounds of Cu(I) or Cu^+

Cuprous oxide, Cu_2O : This is obtained by boiling CuCl with NaOH in the form of a red precipitate. Heating of metallic copper in air also gives Cu_2O. When basic salts of Cu^{+2} e.g., the alkaline solution of $CuSO_4$ in Na-K tartrate (Fehling Solution) is heated with reducing agents such as glucose or an aldehyde, reddish brown precipitate of Cu_2O is obtained :

$$2CuCl + 2NaOH = Cu_2O + 2NaCl + H_2O$$

$$2Cu^{+2} + 2OH^- + 2e^- = Cu_2O + H_2O$$

This reaction is used for testing reducing sugars in the urine of diabetic patients. Cu_2O is used for making red ruby glass. Cu_2O reacts with dilute sulphuric or nitric acids to give the corresponding cupric salts and metallic copper:

$$Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O$$

$$Cu_2O + 2HNO_3 = Cu + Cu(NO_3)_2 + H_2O$$

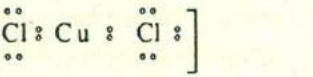
Cuprous chloride, CuCl : This is obtained in the form of a precipitate when copper metal is added to a solution of $CuCl_2$ in presence of HCl. The precipitate of CuCl is formed by oxidation-reduction reaction :

$$CuCl_2 + Cu = 2CuCl$$

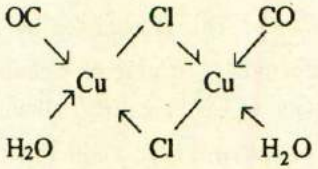
Cuprous chloride is easily produced by dissolving Cu_2O in conc. HCl. CuCl is a white crystalline compound and soluble in conc. HCl giving $CuCl_2^-$:

$$CuCl + HCl = 2HCuCl_2$$

The solution of CuCl in HCl containing $CuCl_2^-$ ion has the two Cl linked to copper by covalent bonds :



CuCl solution in HCl is used in gas analysis for the absorption of CO giving $CuCl.CO.2H_2O$:



Cuprous chloride dissolves in ammonia forming a colourless solution known as *ammonical cuprous chloride*, $Cu(NH_3)_4Cl$. This solution absorbs oxygen and becomes blue due to the conversion of Cu^{+1} to Cu^{+2} and also absorbs CO. With acetylene this gives a bright-red precipitate of cuprous acetylide, Cu_2C_2 :

$$2CuCl + C_2H_2 + 2NH_4OH \rightarrow Cu_2C_2 + 2NH_4Cl + 2H_2O$$

The structure of Cu_2C_2 is, $Cu : C :: C : Cu$

In the vapour state cuprous chloride has the formula Cu_2Cl_2 determined by the vapour density method.

Cuprous iodide, CuI : This is most easily formed when any soluble iodide, such as KI, reacts with copper sulphate solution. Cupric iodide, CuI_2, first formed, is unstable and decomposes into cuprous iodide and free iodine :

$$2CuSO_4 + 4KI = 2CuI + 2K_2SO_4 + I_2$$

This reaction is used for the iodometric determination of copper in solutions by titration of the free iodine or the tri-iodide ion, I_3^-, with sodium thiosulphate according to the reaction :

$$2\,Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

Cuprous thiocyanate, CuSCN : This is obtained in the form of a white precipitate when $CuSO_4$ solution is treated with NH_4CNS or KCNS in presence of SO_2. The green precipitate of $Cu(CNS)_2$ first formed is converted to CuCNS by reduction with sulphurous acid :

$$2Cu^{+2} + HSO_3^- + H_2O = 2\,Cu^+ + HSO_4^- + 2H^+$$

$$Cu^+ + SCN^- = CuSCN$$

This white precipitate is filtered and washed. This is used for gravimetric method for copper determination and also for the separation of copper from zinc which does not form insoluble compound with CNS^- ion.

Compounds of Divalent Copper (Cu^{+2})

As mentioned before the cupric ion has incomplete 3d orbital containing 9 electrons. All its compounds are coloured except anhydrous CuF_2 and $CuSO_4$. The deep coloured compounds or complexes of Cu^{+2} have copper in covalent bonding. Thus, the Cu—O bond in $CuSO_4$ is more ionic in the anhydrous $CuSO_4$ than in $CuSO_4.5H_2O$. In the solid state the divalent copper compounds may be of various colours but the dilute solutions have the blue colour due to the formation of $[Cu(H_2O)_4]^{+2}$ complex ion.

Cupric oxide, CuO : This is obtained when copper metal in finely divided form is heated in oxygen (air). CuO is also formed when cupric nitrate or carbonate is heated strongly as given by the following equations :

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

$$CuCO_3 = CuO + CO_2$$

Cupric oxide is a good oxidising agent and is used to determine carbon in organic compounds.

Copper hydroxide, $Cu(OH)_2$: This is obtained by adding alkali solution to cold solution of cupric salt. In hot condition, CuO is formed. The composition of this precipitate appears to be indefinite. It is somewhat amphoteric and dissolves in excess of concentrated alkali giving a deep blue solution containing cuprate ion, $Cu(OH)_4^{-2}$. The hydroxide precipitate is readily soluble in aqueous ammonia giving a deep blue solution known as "Schwezer's Reagent". This dissolves cellulose and is used for making rayon. The blue solution contains $Cu(NH_3)_4^{+2}$ ions.

Copper sulphate, $CuSO_4$: This is the most important common salt of copper. It is obtained by dissolving CuO or $CuCO_3$ in dil H_2SO_4 and crystallizing :

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

Anhydrous $CuSO_4$ is formed by heating metallic copper in conc. H_2SO_4 :

$$Cu + H_2SO_4 = CuSO_4 + 2H_2O + SO_2$$

Copper sulphate is produced on a large scale by roasting copper pyrites at a controlled temperature. Iron is oxidised to insoluble Fe_2O_3 and $CuSO_4$ is leached

out with water. The leaching on evaporation and crystallization gives the crystals of $CuSO_4.5H_2O$. It is also produced by dissolving scrapes of copper in dil. H_2SO_4 in presence of air :

$$2Cu + 2H_2SO_4 + O_2 = 4CuSO_4 + 2H_2O$$

The oxidative leaching of oxide ore also gives $CuSO_4$:

$$2Cu_2O + 4H_2SO_4 + O_2 = 4CuSO_4 + 4H_2O$$

These reactions are now-a-days used for the extraction of copper from low-grade ores. $CuSO_4$ solution obtained is electrolysed as described before.

The anhydrous copper sulphate is white but when crystallized from aqueous solution, the blue pentahydrate, $CuSO_4.5H_2O$ commonly known as *blue vitriol*, is formed. $CuSO_4.5H_2O$ contains 4 molecules of water co-ordinated to copper and the fifth molecule is attached to the sulphate and also with 2 coordinated water molecules by hydrogen bonding as given in Fig. 15—2. $CuSO_4.5H_2O$, as most of the Cu^{+2} complexes, actually possess distorted octahedral structures containing 4 short and two long metal-to-ligand bonds (see chapter 24).

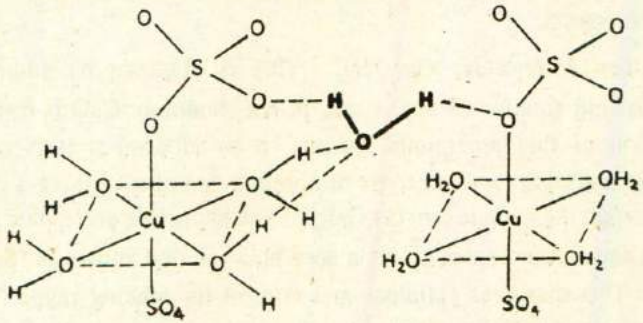


Fig. 15—2. Structure of $CuSO_4.5H_2O$ (two dimensions)

The dehydration of hydrated $CuSO_4$ proceeds in steps giving $CuSO_4.3H_2O$, $CuSO_4.H_2O$ and finally $CuSO_4$ at about 360°C. At high temperature it tends to decompose into CuO and SO_3.

$CuSO_4$ in ammonia solution gives the blue complex $Cu(NH_3)_4SO_4.H_2O$.

$CuSO_4$ is used in electrolytic refining of copper, in electroplating, in making green pigments and as a mordant in the textile industry. This is also used in making Bordeaux Mixture (a mixture of $CuSO_4$ solution and milk of lime) as a wash to kill fungi on plants. It is used to manufacture other compounds of copper. Anhydrous $CuSO_4$ readily takes up water and turns blue

and hence it is used for detecting water in alcohols and ether and also for removing water from these liquids since $CuSO_4.5H_2O$ is insoluble in alcohol and ether.

Copper carbonate, $CuCO_3$: Only basic $CuCO_3$ are formed having compositions $2CuCO_3.Cu(OH)_2$ (deep blue) and $CuCO_3.Cu(OH)_2$ (bright green). They occur in nature as minerals, *azurite* and *malachite* and basic $CuCO_3$ is made by adding limestone to copper nitrate solution.

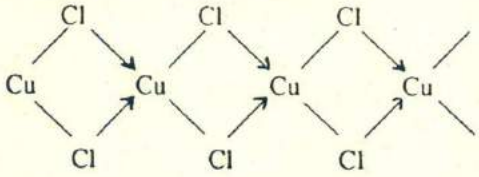
Copper acetate : The basic copper acetate is made by exposing sheets of copper to vinegar and air :

$$2Cu + 2CH_3COOH + O_2 = (CH_3COO)_2Cu.Cu(OH)_2$$

This is only a basic compound and the bright-green substance is known as 'verdigris' and is used as pigments.

Copper chloride : Cupric chloride may be obtained in the anhydrous state by the reaction of copper metal and chlorine. In the hydrated state copper chloride is formed when CuO is dissolved in HCl and the crystalline product is obtained in the form of blue green dihydrate $CuCl_2.2H_2O$.

The anhydrous $CuCl_2$ has chain structures :



In aqueous solutions $CuCl_2$ behaves as strong electrolytes and exhibits tendency to form complex $[CuCl_4]^{-2}$ ions :

$$Cu^{+2} + 4Cl^- \rightleftharpoons [CuCl_4]^{-2}$$

Copper cyanide, $Cu(CN)_2$: This is obtained when potassium cyanide is added to $CuSO_4$ solution as a red precipitate. On boiling, $Cu(CN)_2$ is decomposed forming cuprous cyanide and cyanogen :

$$2Cu(CN)_2 = Cu_2(CN)_2 + (CN)_2$$

Both cuprous cyanide and cupric cyanide are dissolved in excess of KCN forming colourless complexes of composition $K_3Cu(CN)_4$ and $K_2Cu(CN)_4$ respectively. Cuprous compounds generally form $KCu(CN)_2$ complex with KCN, and cupric compounds also give the complex cyanides of cuprous ion

because $Cu(CN)_2$ first formed is readily decomposed to CuCN which actually forms the complex $KCu(CN)_2$ or $K_3Cu(CN)_4$. These cyanide complexes of copper are stable in solution and do not form precipitate of copper sulphide with H_2S whereas Cd complex, $K_2Cd(CN)_4$, is unstable and gives CdS with H_2S. This is the basis of the separation of Cu and Cd.

Copper nitrate, $Cu((NO_3)_2$: This is obtained when metallic copper or CuO is dissolved in dilute HNO_3. The solution on evaporation gives beautiful blue crystals of $Cu(NO_3)_2.3H_2O$ (or $6H_2O$). This is very hygroscopic and on heating decomposes to CuO and NO_2 :

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

Copper thiosulphate, CuS_2O_3 : On adding $Na_2S_2O_3$ solution to $CuSO_4$, a colourless solution is obtained due to the formation of $NaCuS_2O_3$ complex containing Cu^{+1} :

$$CuSO_4 + Na_2S_2O_3 = Na_2SO_4 + CuS_2O_3$$

$$2CuS_2O_3 + 2Na_2S_2O_3 = 2NaCuS_2O_3 + Na_2S_4O_6$$

But the solution of $NaCuS_2O_3$ is unstable and is decomposed to give Cu_2S on warming :

$$2NaCuS_2O_3 + H_2O = Cu_2S + Na_2S_2O_3 + H_2SO_4$$

Complex Compounds of Copper

A large number of complex compounds of both Cu^+ and Cu^{+2} have been described above. The most common complexes are :

$[Cu(NH_3)_4]^{+2}$, $[Cu(H_2O)_4]^{+2}$
$[CuCl_3]^-$, $[CuCl_4]^{-2}$, $[Cu(CN)_4]^{-2}$
$[Cu(NH_2—CH_2—CH_2—NH_2)_2]^{+2}$ $NaCuS_2O_3$ etc.

Organic acids form large number of complexes with Cu^{+2}. The complexes of Cu^{+1} are tetrahedral in structure but Cu^{+2} complexes are distorted octahedral although they appear to be square planar.

Fehling Solution :

In presence of tartrate ion, $C_4H_4O_6^{-2}$, copper sulphate forms an intense blue solution from which copper cannot be precipitated, as $Cu(OH)_2$ by alkali. The

alkaline solution of $CuSO_4$ with potassium hydrogen tartrate, $KHC_4H_4O_6$, is known as *Fehling Solution*. This is used to detect the presence of reducing sugars, such as glucose. The copper complex has probably the structure as shown in Fig. 15—3.

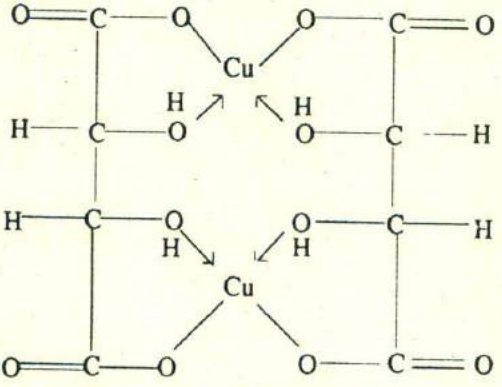


Fig. 15—3. Copper tartrate complex in Fehling Solution.

Compounds of Silver

Silver oxide, Ag_2O : This is formed in a number of ways. Usually it is made by the action of alkalies on silver nitrate solution. A dark brown precipitate of Ag_2O is formed :

$$2AgNO_3 + 2NaOH = Ag_2O + 2NaNO_3 + H_2O$$

Ag_2O is sparingly soluble in water; the solution is distinctly alkaline due to the reaction :

$$Ag_2O + H_2O \rightleftharpoons 2Ag^+ + 2OH^-$$

Silver oxide readily dissolves in aqueous ammonia to form a strong base which is a colourless complex, $Ag(NH_3)_2OH$. This solution behaves as a weak oxidizing agent. This reacts with aliphatic and aromatic aldehydes reducing $[Ag(NH_3)_2]^+$ ion to metallic silver which deposits in the form of mirror. $[Ag(NH_3)_2]OH$ is known as *Tollens' Reagent.*

$$2Ag(NH_3)_2OH + RCHO \longrightarrow RCOONH_4 + 3NH_3 + H_2O + 2\,Ag$$

On heating, Ag_2O is readily decomposed to metallic silver in presence of air. Hence the case of extracting silver by roasing of its ores :

$$2Ag_2O = 4Ag + O_2$$

In presence of alkaline solution, Ag^{+1} is oxidised to Ag^{+2} and Ag^{+3} by strong oxidising agents forming AgO and Ag_2O_3.

Ag_2O is a good reagent for preparing soluble hydroxides from halides. It is used both in organic and inorganic chemistry. Thus, cesium chloride reacts with Ag_2O to form soluble CsOH and AgCl which is removed by filtration :

$$2CsCl + Ag_2O + H_2O = 2CsOH + 2AgCl$$

Silver halides, AgX : Silver fluoride, AgF, is extremely soluble in water whereas the chloride, bromide and iodide are insoluble. The curdy precipitates of silver halides are obtained when $AgNO_3$ is added to soluble halides. Thus,

$$AgNO_3 + NaX \rightarrow AgX + NaNO_3$$

AgF is obtained by dissolving Ag_2O in HF and by crystallization. The colour of the various silver halides are different.

Ag X	*Colours*	*Solubility in H_2O*	*Solubility in NH_4OH*
AgF	white	soluble	soluble
AgCl	white	insoluble	soluble
AgBr	pale yellow	insoluble	difficultly soluble
AgI	pale brown	insoluble	insoluble

Many of the silver salts are insoluble in water except $AgNO_3$, $AgClO_4$ and AgF. Most silver salts are also colourless but those containing polarizable anions are coloured as well as insoluble. AgI, Ag_3AsO_4, Ag_2CrO_4 Ag_3PO_4 are coloured. The small Ag^{+1} ion has great polarizing action on large I^- ion and, according to Fajan's rule, AgI is considered as a covalent compound.

The solution of AgX in ammonia gives complex $Ag(NH_3)_2X$.

Silver halides are affected by light and turn dark in colour because of the reduction into their elements :

$$2AgX + light\ (h\nu) = 2Ag + X_2$$

This fact has been used in large scale applications of silver halides in the production of photographic films.

Silver nitrate, $AgNO_3$: This is obtained by dissolving silver metal in HNO_3 and crystallising $AgNO_3$ by evaporation :

$$3Ag + 4HNO_3 = 3AgNO_3 + 2H_2O + NO$$

$AgNO_3$ is the only simple salt of Ag which is of great use in solution. The solution of $AgNO_3$ in water is neutral and not hydrolysed. This indicates that Ag_2O is a strong base.

$AgNO_3$ is produced on a commercial scale under the trade name "Lunar caustic". Organic substances readily reduce $AgNO_3$ to give free Ag. For instance, the black stains on skins and clothes are due to the deposition of silver from $AgNO_3$ by reduction. $AgNO_3$ is mostly used in producing photographic films and mirrors and as a laboratory reagent.

Complex Compounds of Silver

Silver forms a large number of complexes as in the case of copper. Silver salts dissolve in KCN and NH_4OH to form soluble colourless complexes :

Amino complexes of silver : Many insoluble silver compounds dissolve readily in aqueous ammonia forming amino-silver complexes. Thus Ag_2O which is formed by adding a base to a silver salt dissolves in NH_4OH solution to give $[Ag(NH_3)_2]^+$ ion :

$$Ag_2O \text{ (solid)} + 4\ NH_3 + H_2O \rightarrow 2\ [Ag(NH_3)_2]^+ + 2OH^-$$

Solutions of silver salts in ammonia are used in silver plating. Evaporation of a solution containing $[Ag(NH_3)_2]^+$ ions leaves dangerous residues which explode violently and are supposed to contain silver amide, $AgNH_2$, and silver azide, AgN_3. This indicates that bonds between Ag—N are of different type. This is represented as,

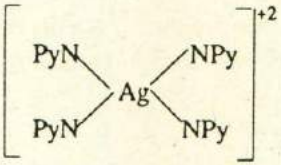
$$[H_3N \rightarrow Ag \leftarrow NH_3]^+$$

Ammonical $AgNO_3$ solution produces beautiful mirror of silver with reducing agent, such as glucose, when warmed. This reaction is used for producing mirrors on industrial scale.

With KCN silver salts form $[Ag(CN)_2]^-$; the thiosulphate complex, $[Ag(S_2O_3)_2]^{-3}$, is formed during the fixing process of photography by dissolution of AgBr in $Na_2S_2O_3$.

Divalent compounds of silver : There are some Ag^{+2} compounds formed by special reactions. AgF_2 is formed when fluorine gas is passed over silver powder or by the action of ClF_3 on AgCl. Argentic oxide, AgO, is formed by precipitation from $AgNO_3$ solution with potassium persulphate, $K_2S_2O_8$,

or by oxidising Ag_2O with hot alkaline $KMnO_4$, solution. Stable complexes of divalent Ag contain Ag atom bonded to four or more N atoms in the complexing groups, e.g., 2—2—dipyridyl complex of Ag^{+2}. Dipyridyl N atoms are bonded to Ag^{+2} as shown below :



Divalent complexes, like those of copper, have an odd electron and is highly coloured having magnetic properties. Ag^{+2} has great oxidizing power and does not exist in aqueous solutions.

The Processing of Photographic Films

1. The photographic films : Photographic films are thin sheets of cellulose acetate or other polymer films coated with a colloidal suspension of small silver halide crystals in gelatin. Pure solutions of silver nitrate, potassium bromide and potassium iodide are mixed in the presence of gelatin for the preparation of the photographic emulsion. The particle size and the amounts of silver halides are used to determine the "sensitivity" or "speed" of the film.

2. Exposure : The film is exposed when the image is focussed upon the light-sensitive photographic emulsion on the film. The silver crystals become "activated" when exposed to light and they become reduced. The chemical change is not well understood, but the silver halide crystals receive the most light (from the lighted areas of the object) and are more readily reduced than those-receiving little light (from the dark areas of the object), during the development of the film.

3. Developing : After exposure, the film is developed by placing it in an alkaline solution of an organic reducing agent, such as hydroquinone or pyrogallol. The reducing agent acts upon the grains of silver halide with a speed proportional to the intensity of the illumination during exposure and reduces them to metallic silver :

$$AgX + e^- \text{ (reducing agent)} \longrightarrow Ag + X^-$$

4. Fixing : After developing, the film is fixed by treating it with a solution of sodium thiosulphate (hypo) to dissolve the unreduced silver halide :

$$AgX + 2Na_2S_2O_3 \rightleftharpoons Na_3Ag(S_2O_3)_2 + NaX$$

The metallic silver remaining on the film forms the visible image and is called a negative, since the bright portions of the original image are now dark and the dark portions of the original are now bright.

5. Printing : The printing process is essentially the same as that of making a negative. Since the sensitive printing paper is illuminated through the negative, the image is once again reversed, and now corresponds to the original image as regards bright and dark areas on the print.

6. Toning : The printing may be toned by replacing part of the silver of the image by gold or platinum. To do this, the print is treated with solutions of $NaAuCl_4$ or K_2PtCl_6. The more active silver displaces these noble metals from their salts to give a thin deposit of gold (red tone) or platinum (dark gray).

Compounds of Gold

Gold forms two series of compounds having Au^+ and Au^{+3} oxidation states. A good example is the compounds obtained by dissolving gold in aqua regia :

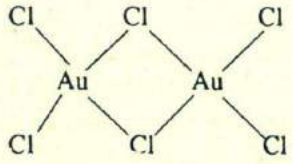
$$Au + \text{Aqua regia } (HNO_3 + HCl) \longrightarrow \text{Solution}$$

$$\text{Solution} \xrightarrow{\text{evaporation}} HAuCl_4.4H_2O \text{ (Chlorauric acid } (Au^{+3}))$$

$$AuCl \xleftarrow{\text{heat}} AuCl_3\ (Au^{+3}) \xleftarrow[-HCl]{\text{heated}} HAuCl_4.4H_2O$$

$$AuCl \xrightarrow{\text{heat}} Au \text{ (metal)}$$

All compounds of gold are decomposed by heat because of their thermal instability. AuCl undergoes disproportionation reactions forming $AuCl_3$ and Au. $AuCl_3$ has 4 bonds per gold atom having the structure :



$Au(OH)_3$ formed by precipitation is a weak base and dissolves in hot KOH to form potassium aurate, $KAuO_2$.

A large number of complexes of gold is known. Univalent gold gives $KAu(CN)_2$ and Au^{+3} gives $KAu(CN)_4$. These are used in the extraction of gold and in gold-plating.

Gold fulminate, $Au(N_2H_3)$ is obtained by ammonolysis when $AuCl_3$ is treated with ammonia. This explodes violently on heating :

$$AuCl_3 + 2NH_3 = Au\begin{matrix}\diagup NH_2 \\ \diagdown\!\!\diagdown NH\end{matrix} + HCl$$

QUESTIONS AND PROBLEMS

1. How does gold show a variable oxidation states? Explain the disproportionation of Au^+ compounds.
2. Discuss the principle involved in the extraction of gold by the cyanide process.
3. Describe the electrolytic refining of copper.
4. How do you explain the stability of Cu^{+1} and Cu^{+2} compounds ?
5. What happens when Cu salts are dissolved in (i) aqueous ammonia; (ii) KCN solution; (iii) tartaric acid solution and (iv) strong solution of NaOH?
6. (a) Discuss briefly the principles underlying the extraction of copper from its sulphide ore.

   (b) How is copper obtained in the pure conditions ?

   (c) Mention the composition and use of three important alloys of copper.
7. Compare the chemistry of copper and silver.
8. What are the advantages of the process of electroplating ? Explain in detail the method for silver plating.
9. How is copper extracted from sulphide ores ? Describe the method adopted for very poor ores. Describe copper ion complexes and its important alloys.

4. Fixing : After developing, the film is fixed by treating it with a solution of sodium thiosulphate (hypo) to dissolve the unreduced silver halide :

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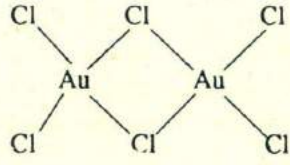
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$$\text{Solution} \xrightarrow{\text{evaporation}} HAuCl_4.4H_2O \text{ (Chlorauric acid } (Au^{+3}))$$

$$HAuCl_4.4H_2O \xrightarrow{\text{heated, -HCl}} AuCl_3 \ (Au^{+3}) \xrightarrow{\text{heat}} AuCl \xrightarrow{\text{heat}} Au \text{ (metal)}$$

All compounds of gold are decomposed by heat because of their thermal instability. AuCl undergoes disproportionation reactions forming $AuCl_3$ and Au. $AuCl_3$ has 4 bonds per gold atom having the structure :



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8. What are the advantages of the process of electroplating ? Explain in detail the method for silver plating.
9. How is copper extracted from sulphide ores ? Describe the method adopted for very poor ores. Describe copper ion complexes and its important alloys.

10. Explain electroplating with reference to gold plating.
11. Describe the occurrence and extraction of copper from its ores. Name the most important alloys of copper and give their compositions and uses.
12. Write a note on the occurrence and extraction of either silver or gold.
13. Write notes on; (a) electroplating and (b) silvering of mirrors.
14. Give a comparative study of the chemistry of copper, silver and gold and their principal compounds.

    Justify their inclusion in the same group of the Periodic Table with the alkali metals.
15. (a) Explain the process of hydrometallurgy of copper.

    (b) What are Fehling solution and Tollen's Reagent? Compare their actions on reducing substances.
16. What are coinage metals ? From a study of the properties of coinage metals and their compounds, justify their inclusion in the same group of the Mendellef's Periodic Table. Mention some important applications of the coinage metals.
17. Write short notes on :

    (a) The cyanide process for extraction of gold.

    (b) Reactions involved in copper metallurgy.
18. What are the sources of gold ? Describe in detail the cyanide process for the extraction of gold.
19. Write brief accounts on electro-refining of gold.
20. Discuss : (i) Properties of coinage metals are different from those of the alkali metals.

    (ii) Copper can be determined iodometrically.
21. A certain hydrate analyzes as follows : Cu—29.7%, H—2.8%, S—15.0% and O—52.5%. Determine the empirical formula of the hydrated compound.
22. A chemist wants to calculate Avogadro Number by the inspection of a solid cube of AgCl. The density of the cube is 5.56 g/cm^3. The spacing between the Ag^+ and Cl^- ions in the cube is 2.773 Å from their centres. Calculate the Avogadro's Number.
23. How is it possible to float the copper bearing particles in an ore of copper to the surface of a tank of water ?
24. List the major steps in the refining of copper. For what purposes copper is used ?
25. List the unique properties of Cu, Ag and Au that allow their extensive use as coinage metals.

CHAPTER 16

THE ALKALINE EARTH METALS

(Elements of Group II A)

The elements of group II are divided into two sub-groups, A and B. The elements of group IIA are known as *Alkaline Earth Metals.*

Group II A	Group II B
Be — Beryllium*	
Mg — Magnesium	
Ca — Calcium	Zn — Zinc
Sr — Strontium	Cd — Cadmium
Ba — Barium	Hg — Mercury
Ra — Radium	

The Electronic Structure

The metals of Group IIA, that is, Be, Mg, Ca, Sr, Ba and Ra have two electrons in the outermost energy level. These two electrons are very well screened by the nuclear charges which are similar to those of the alkali metals. The electronic configurations of IIA metals are given in Table 16.1. Each of the alkaline earth metals has two electrons in the valence shell which is just outside

Table 16.1. Electronic configuration of the alkaline earth metals.

At No. Z	*Elements*	*Electronic structure*	*Valence electrons*
4	Be	He core, $2s^2$	$2s^2$
12	Mg	Ne core, $3s^2$	$3s^2$
20	Ca	Ar core, $4s^2$	$4s^2$
38	Sr	Kr core, $5s^2$	$5s^2$
56	Br	Xe core, $6s^2$	$6s^2$
88	Ra	Rn core, $7s^2$	$7s^2$

* Old name of Be is glucinum because all its salts have sweet taste.

an inert gas core. It is seen that alkaline earth metals are not the only elements with 2 electrons in the outermost energy level. It will be interesting to distinguish these elements here for the sake of an understanding of their chemical properties in relation to the alkaline earth metals.

Elements	*Outermost valence shell*
Helium—	s^2 (Stable state)
Alkaline earth metals—	s^2 (Valence electrons)
Transition elements—	s^2 (Part of valence electrons)
Zn, Cd, Hg (group II B)—	s^2 (Valence electrons)
Lanthanides and Actinides—	s^2 (Part of valence electrons)

Thus, the electron grouping of s^2 in the outermost energy level of the above group of elements occur in each case, but the chemistry is vastly different in certain cases. The electrons in the inner orbitals also play a very important part in determining the nature of an element or groups of elements.

Physical Properties

The two outermost s electrons of alkaline earth metals resonate and thus form covalent bond between each atom and its adjacent atoms in the crystal lattice. Like alkali metals these electrons move through metallic network under electrical potential. The metals are, therefore, good conductors of electricity and heat. The silvery appearance of a freshly cut surface is due to the presence of the s electrons reflecting light. Because there are two electrons instead of one, the bonds between the atoms are stronger and hence the alkaline earth metals are harder and heavier than the alkali metals. Beryllium is hard enough to scratch glass. The alkaline earth metals also have higher melting points for the same reason. Some of the physical properties of the alkaline earth metals are given in Table 16.2

As the radius of the atom of the alkaline earth metals increase, the ease of removing the outer electrons is also increased and hence the reactivity of the metals increase with the atomic number. The values of the ionization potentials

Table 16.2. Physical properties of alkaline earth metals.

Properties	*Be*	*Mg*	*Ca*
Atomic Number	4	12	20
Atomic radius (Å)	0.90	1.36	1.74
Ionic radius, M^{+2} ion (Å)	0.31	0.65	0.99
Ionization potential (ev)	9.30	7.60	6.10
Electronegativity	1.50	1.20	1.00
Density (g/cm^3)	1.86	1.75	1.55
Melting point (°C)	1280	651	851
Boiling point (°C)	1500	1100	1487
Electrode potential (v)	Be/Be^{+2} 1·7	Mg/Mg^{+2} 2·34	Ca/Ca^{+2} 2.87
Oxidation states	+2	+2	+2
Heat of hydration M^{+2} (aq.) (Kcal/g.ion)	570	460	395
Properties	*Sr*	*Ba*	*Ra*
Atomic number	38	56	88
Atomic radius (Å)	1.91	1.98	2.20
Ionic radius, M^{+2} (Å)	1.13	1.35	1.52
Ionization potential (ev)	5.70	5.20	5.20
Electronegativity	1.00	0.90	0.97
Density (g/cm^3)	2.60	3.59	6.00
Melting point (°C)	770	710	960
Boiling point (°C)	1366	1537	1150
Electrode potential (v)	Sr/Sr^{+2} 2·89	Ba/Ba^{+2} 2·90	Ra/Ra^{+2} 2.92
Oxidation states	+2	+2	+2
Heat of hydration M^{+2} (aq.) (Kcal/g.ion)	355	305	—

and the electrode potentials signify the same trend in the reactivity. Be, the first element in group IIA, is a bridge element and resembles Al in group IIIA. Magnesium is also somewhat different from Ca, Sr and Ba. Thus the hydroxides of Be and Mg are almost insoluble in water and $Be(OH)_2$ is amphoteric whereas the hydroxide of Ca, Sr and Ba are strongly basic and soluble in water. This is due to small size of Be and Mg which have tendency to form oxides and

hydroxides and other compounds which are more covalent than those of the heavier and large-sized Ca, Sr and Ba atoms, Complexes of Be are quite numerous and stable but others show less tendency to form stable complexes. The solubility of carbonates and sulphates of the alkaline earth metals decreases considerably with the increase in the ionic sizes from Be to Ra.

An interesting feature regarding the trend in the group is observed in the temperature of decomposition of their carbonates to MO and CO_2.

Compounds	*Temperature of decomposition* °C
$BeCO_3$	90
$MgCO_3$	540
$CaCO_3$	900
$SrCO_3$	1290
$BaCO_3$	1360

As in the case of alkali metal carbonates, the CO_3^{-2} has a resonating structure and the metal is bonded to an oxygen of CO_3^{-2} either by ionic bond or gradual increase of covalent bond as the charge on M increases. The most stable carbonates have purely ionic bond. Increase of charge and decrease of size of M produces polarization effect with oxygen of the carbonate resulting in the formation of M—O bond and release of CO_2.

The term 'alkaline earth' was formerly used to denote oxides of Ca, Sr and Ba because of their resemblance with Al_2O_3 which is a typical "earth" and due to the fact that they produce alkalis in water. The term 'alkaline earth' has now been extended to include Be and Mg. Radium has quite similar chemistry particularly to that of Ba but is radioactive.

Chemical Properties

(a) Reaction with air (O_2 and N_2) : The alkaline earth metals react readily on heating with oxygen and nitrogen of the air to form oxides, MO, and nitrides, M_3N_2. Pure oxygen gives oxides. Be reacts less rapidly and requires high temperatures for the formation of BeO which is covalent and others are ionic. Ba forms peroxides, BaO_2, because of its greater reactivity. Be does not form peroxides.

(b) Reaction with hydrogen : Ca, Sr and Ba react with hydrogen when heated to produce crystalline ionic hydrides. These hydrides readily react with water to give hydrogen :

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$$

(c) Reaction with nitrogen : Alkaline earth metals form M_3N_2 on hearing in presence of nitrogen. These are hydrolysed by water to give ammonia :

$$Mg_3N_2 + 6\,H_2O = 3Mg(OH)_2 + 2NH_3$$

(d) Reaction with water : The Alkaline earth metals react readily with water giving off H_2 and forming $M(OH)_2$. Mg and Be do not react with water readily. The electrode potential of Be is much lower than the other alkaline earth metals.

(e) Reaction with acids : They react vigorously with acids forming the corresponding salts.

(f) Reaction with halogens: The alkaline earth metals form halides, MX_2, by direct reaction with halogens. Beryllium halides are covalent whereas other halides of the group are ionic. These halides are readily soluble in water except the fluorides of Mg, Ca, Sr and Ba. Alkaline earth metal halides form hydrates.

Comparison of the Alkali and the Alkaline Earth Metals

The alkali and alkaline earth metals have quite a good deal of resemblance in their properties. The reason for this is the same outermost energy level involved for the valence electrons shown below :

Z	*Alkali metals*			*Z*	*Alkaline Earth metals*		
3	Li	(2)	$2s^1$	4	Be	(2)	$2s^2$
11	Na	(10)	$3s^1$	12	Mg	(10)	$3s^2$
19	K	(18)	$4s^1$	20	Ca	(18)	$4s^2$
37	Rb	(36)	$5s^1$	38	Sr	(36)	$5s^2$
55	Cs	(54)	$6s^1$	56	Ba	(54)	$6s^2$
87	Fr	(86)	$7s^1$	88	Ra	(86)	$7s^2$

The points of similarity are :

(1) Like alkali metals, they are electropositive and have great chemical activity. They do not occur in the free state in nature.

(2) Both are extracted by electrolytic methods from their stable salts such as chlorides.

(3) Both are soft, silvery white in untarnished conditions.

(4) React with water to give metal hydroxides and H_2.

(5) The hydroxides give strong bases with water.

The points of the contrast between the alkali and alkaline earth metals arise mainly due to the presence of 2 valence electrons in the case of alkaline earth metals and 1 valence electron in the case of alkali metals. It is noted that M^{+2} and M^{+1} ions have the some electronic configurations as in the case of K^+ and Ca^{+2} as given below :—

$$K \quad — \quad 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$$

$$K^+ \quad — \quad 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$$

$$Ca \quad — \quad 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$$

$$Ca^{+2} \quad — \quad 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$$

But the excess positive charge of M^{+2} pulls the electron cloud closer to the nucleus than in M^{+1}. Hence there is greater decrease in size in M^{+2} than in M^{+1}. Moreover, the s^1 and s^2 electrons give rise to the differences in the physical characteristics of the two metals.

Some of the points of contrasts are :

(1) The alkaline earth metals are harder, heavier and have higher melting points than those of alkali metals.

(2) Increased charge and smaller size of M^{+2} give rise to greater polarizing capacity than the alkali metals. Hence the oxides and hydroxides of M^{+2} have more covalent character and are less basic as compared to the alkali metals. The covalent character is more pronounced in the case of Be and Mg compounds

because of their smaller ionic sizes which have stronger polarising effect on anions.

(3) Ca, Sr and Ba react less vigorously with water than alkali metals. Be and Mg can survive in contact with water for a long time.

(4) Carbonates and sulphates of alkaline earth metals are insoluble in water whereas those of alkali metals are soluble and undergo hydrolysis (except Li_2CO_3 which is insoluble).

(5) Phosphates of alkaline earth metals are insoluble whereas those of alkali metals are soluble (except Li_3PO_4 which is insoluble).

Occurrence of the Alkaline Earth Metals

Calcium is one of the most abundant elements and is widely distributed in nature in he form of limestone which is impure calcium carbonate. Calcium also occurs in the form of $CaSO_4.2H_2O$ known as *gypsum* and *fluorspar*, CaF_2. Magnesium is found in carnallite, $MgCl_2.6H_2O$ and in dolomite, $CaCO_3.MgCO_3$. Beryllium occurs in *beryl*, an alumino silicate, $Be_3Al_2(SiO_3)_6$. Strontium is rare and the chief ore is *celestite*, $SrSO_4$. Barium is more abundant and is found in *barite* or heavy spar, $BaSO_4$, and also as $BaCO_3$. Radium is found in *pitchblende and cleveite*.

Metallugry of Alkaline Earth Metals

Extraction of Beryllium :

Sources : Beryl—$Be_3Al_2(SiO_3)_6$

Chrysoberyl—$BeAl_2O_4$

Extraction Process : The ore beryl is first processed to get $BeCl_2$, BeF_2 or BeO. The halides of Be are subjected to electrolysis in the fused state in presence of a conducting salt such as NaCl or NaF. BeO is reduced to Be in an electric arc furnace by means of carbon.

1. Reduction of BeO in electric are :

$$\text{Powdered beryl} + K_2CO_3 \xrightarrow{\text{fused}} \text{fused mass}$$

$$\text{fused mass} \xrightarrow{\text{conc. } H_2SO_4} \text{sulphate ore}$$

$$\text{sulphate ore} \xrightarrow[\text{(leached)}]{H_2O} BeSO_4 \xleftarrow{\text{evaporated}} \text{solid } BeSO_4$$

$$\text{solid } BeSO_4 \xrightarrow{\text{ignition}} BeO$$

$$BeO + C \xrightarrow[\text{electric arc}]{\text{heated in carbon pot}} Be + CO$$

2. Electrolytic method from BeO :

$$BeO + Cl_2 \xrightarrow{\text{heat}} BeCl_2 + CO\uparrow$$

$$BeCl_2 \xrightarrow{+ NaCl,\ \text{heat}} \text{Fused mass}$$

$$\text{Fused mass} \xrightarrow{\text{electrolysed}} Be \text{ (metal)}$$

3. Ground ore (beryl) $+ Na_2SiF_6 \xrightarrow[\text{fused}]{850°C} Na_2BeF_4 + Na_3AlF_6$

$$Na_2BeF_4 + Na_3AlF_6 \xrightarrow{H_2O} \begin{cases} Na_2BeF_4 \text{ solution} \\ Na_3AlF_6 \text{ insoluble} \end{cases}$$

$$Na_2BeF_4 \text{ solution} \xrightarrow{\text{evaporated}} 2NaF.BeF_2$$

$$2NaF.BeF_2 \xrightarrow{\text{heat, } + NaF, + BaF_2 \text{ (flux)}} \text{Fused mass}$$

$$\text{Fused mass } (1400°C) \xrightarrow[\substack{\text{C—cathode} \\ \text{Fe—anode}}]{\text{electrolysed}} Be \xrightarrow[2000°C]{\text{sublimed}} \text{pure Be metal}$$

Extraction from Liquid NH_3 : Small quantities of Be is obtained in a very pure state by electrolysing $BeCl_2$ or $Be(NO_3)_2$ in liquid NH_3.

Magnesium

Sources : Magnesite — $MgCO_3$

Dolomite — $MgCO_3.CaCO_3$

Carnallite — $MgCl_2.KCl.6H_2O$

Asbestos — $H_4Mg_3Si_2O_9$

Extraction Process : Magnesium is extracted by the electrolysis of $MgCl_2$ or from MgO. Megnesium chloride used may be obtained from $MgCO_3$. By thermal decomposition, $MgCO_3$ is converted to MgO which when heated with CO and Cl_2 gives anhydrous $MgCl_2$:

$$MgCO_3 = MgO + CO_2$$
$$MgO + CO + Cl_2 = MgCl_2 + CO_2$$

$MgCl_2$ in the hydrated form, $MgCl_2.2H_2O$, may be obtained from sea water or carnallite by precipitation of Mg^{+2} with slaked lime, $Ca(OH)_2$. The precipitate of $Mg(OH)_2$ is dissolved in HCl and the solution is evaporated to $MgCl_2.2H_2O$. This, on heating in presence of dry HCl gas, gives $MgCl_2$.

The fused carnallite, $MgCl_2.KCl$, may also be used for the extraction of Mg by electrolysis process.

(1) The electrolytic vessel is a cast iron tank which is also made the cathode. A covered anode is made of graphite which dips in the fused $MgCl_2$ (containing NaCl or KCl to lower the fusion temperature and increase the conductivity) as shown in Fig. 16—1. The Cl_2 gas produced during the electrolysis escapes from the opening in the anode porcelain hood. The electrolysis is carried at a temperature of 700°C in an inert atmosphere (coal gas or H_2)). The molten Mg metal formed at the cathode rises to the surface of the fused mixture and is collected. The purity of Mg is about 99.9% which is purified further by heating in a flux of $MgCl_2$ and NaCl.

(2) Mg can also be obtained directly from MgO by electrolytic method as in the case of Al from Al_2O_3. MgO is dissolved in a fused mixture of BaF_2, MgF_2 and NaF. The electrolysis is done with iron cathode and graphite anode in a steel

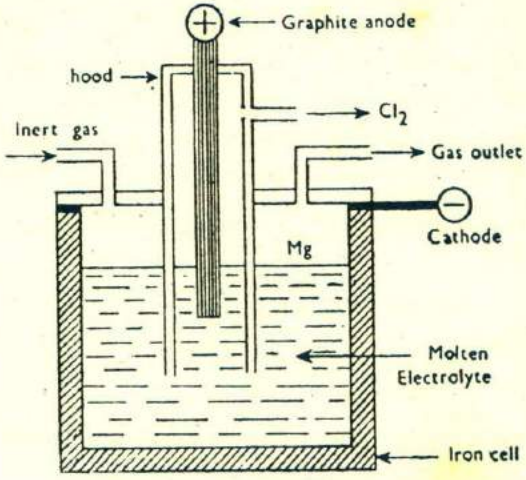


Fig. 16—1. Electrometallurgy of magnesium

tank at a temperature of 950C. Mg is liberated at the cathode and O_2 at the anode.

MgO can be directly converted to Mg by heating with C at a temperature of 2000°C :

$$MgO + C = Mg + CO$$

Mg vaporises with CO and reoxidation of Mg is prevented by means of H_2 gas or coal gas in the reaction vessel and cooled rapidly to solidify Mg.

(3) Mg has been recently obtained by heating MgO with ferrosilicon under reduced pressure :

$$MgO + Fe = Mg + FeO$$
$$2MgO + Si = 2\,Mg + SiO_2$$

FeO forms a slag with SiO_2 giving $FeSiO_3$ which is easily removed.

Calcium, Strontium and Barium

Source of Ca :

Limestone, chalk, marble —	$CaCO_3$
Gypsum —	$CaSO_4.2H_2O$
Fluorspar—	CaF_2
Phosphorite—	$Ca_3(PO_4)_2$

Extraction of Ca : The mineral $CaCO_3$ is converted to $CaCl_2$ which is subjected to electrolysis in the fused state mixed with an alkali metal halide or CaF_2 using iron catode and graphite anode. The iron cathode is slowly raised as the liberated Ca collects at the tip of the cathode. The calcium is only 85% pure and is distilled in high vacuum to make it pure.

Strontium : This is obtained by electrolysis of fused $SrCl_2$ with KCl as in the case of Ca.

Barium : This may be obtained by the electrolytic method of fused $BaCl_2$. Electrolysis of $BaCl_2$ solution using Hg cathode has also been in use. Ba amalgam formed is distilled to remove Hg.

[N. B. Radium is treated separately in this book, see Chapter 27]

Uses of Alkaline Earth Metals

Uses of Be : 1. It is transparent to X-rays and the metal is used for window material in X-ray tubes.

2. Be is used in the manufacture of light alloys, such as Be—Cu and Be—Ni resistant to salt water corrosion.

Uses of Mg : 1. Mg has great reducing property and combines with oxygen and is used to separate non-metals, such as Si, B from their oxides. Burning Mg combines with O of CO_2 liberating C :

$$2Mg + CO_2 = 2MgO + C$$

2. It is used in photoflash bulbs because it emits brilliant light and also used in military flares.

3. Light-weight alloys of Mg with special properties are made. These are :

Magnalium (Mg—90%, Al—9% and Cu—1%). It is hard, strong and light and is used in aeroplane engines, speed boats etc.

Electron (Mg—95% and Zn—5%). It is also a light alloy and has special properties.

Uses of Ca : 1. Ca is used as a dehydrating agent for organic solvents, such as alcohols.

2. As a scavenger to remove gases in fused metals.

3. As a reducing agent in the production of Cr, Th etc.

Uses of Ba : 1. Ba is used as a degassing agent in making vacuum tubes.

2. Ba—Ni alloys are used in vacuum tubes and spark plugs.

[**N. B.** Strontium has no significant use, its compounds are used in pyrotechniques.]

Compounds of Alkaline Earth Metals

Some important compounds of alkaline earth metals are described with regard to their commercial uses and scientific studies.

Compounds of Be

Compounds of Be even with O and F have greater covalent character.

Beryllium oxide, BeO : This is formed by igniting $BeCO_3$.

BeO is hard and insoluble in water. It dissolves both in acids and alkalies to show its amphoteric character :

$$2\,BeO + 2HCl = Be_2OCl_2 + H_2O$$

$$BeO + 2NaOH + H_2O = Na_2Be(OH)_4$$

BeO is extremely poisonous and its use in fluorescent tube has been abandoned. BeO crystal consists of BeO_4 tetrahedra.

Beryllium hydroxide, $Be(OH)_2$: This is formed as a precipitate by adding ammonia to a Be-salt solution. Caustic alkalis dissolve it forming clear solution. This is also soluble in acids and shows amphoteric character :

$$Be(OH)_2 = Be^{+2} + 2\,(OH)^-$$

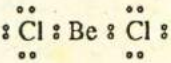
$$Be(OH)_2 + 2H_2O = 2H_3O^+ + BeO_2^{-2}$$

Beryllium halides, BeX_2 : When chlorine is passed over a heated mixture of BeO and C, $BeCl_2$ is obtained. This sublimes as white crystals. Beryllium halides are easily hydrolysed and in this respect it resembles Al^{+3} salts and forms an acid solution :

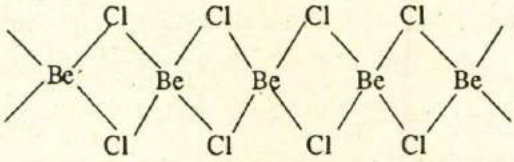
$$BeCl_2 + 2H_2O = Be(OH)_2 + 2HCl$$

$BeCl_2$ is a linear molecule indicating the use of sp hybrid orbitals by Be to form two equivalent bonds at an angle of 180°. The properties of Be compounds indicate covalent bonding with Be. The electronic structure of Be is $1s^2 2s^2$. At

first sight it appears that Be may not form any compound and may behave like an inert gas. But by invoking the mechanism of promotion of electron to higher energy level as in the case of carbon, one of the 2s electrons of Be may be placed in a 2p orbital giving the excited state $1s^2\ 2s^1\ 2p_x^1$. The two unpaired electrons form two bonds but these two bonds of Be must be different from one another because one bond is formed by $2s^1$ electron and the other by $2p_x^1$ electron through sharing of electrons or overlap of orbitals with 2 other atoms such as those of Cl. But the two bonds of Be are completely identical in length and strength and are linear. It is, therefore, concluded that Be does not use the $2s^1$ and $2p_x^1$ electron orbitals separately but a combination of the two forming sp hybrid bond orbitals which are equivalent and collinear. Thus in $BeCl_2$, the bonds between Be and 2Cl are formed by overlap of p orbitals of Cl atoms with sp hybrid orbitals of Be as given in Fig. 2—9 (page 78). The same structure for $BeCl_2$ is proved by the repulsion of two electron pairs which form the bonds. The gaseous $BeCl_2$ is a linear molecule.



But in most solid compounds Be occupies the tetrahedral positions indicating sp^3 hybrid bond formation. Thus, solid $BeCl_2$ is a polymer molecule in which each Be is surrounded by 4Cl :



Beryllium alkyls also show similar structures as in the case of $Be(CH_3)_2$, $Be(C_2H_5)_2$ etc.

Basic Beryllium acetate, $Be_4O(C_2H_3O_2)_6$: This is obtained by the reaction of $Be(OH)_2$ with CH_3COOH and evaporation. It is an interesting compound having the four beryllium atoms situated at the corners of a regular tetrahedron and oxygen at the centre. The six edges are occupied by the acetate

groups, Fig. 16—2 (a). [Compare from the structure of Be—oxalate Fig. 16—2. (b) in which Be is at the centre].

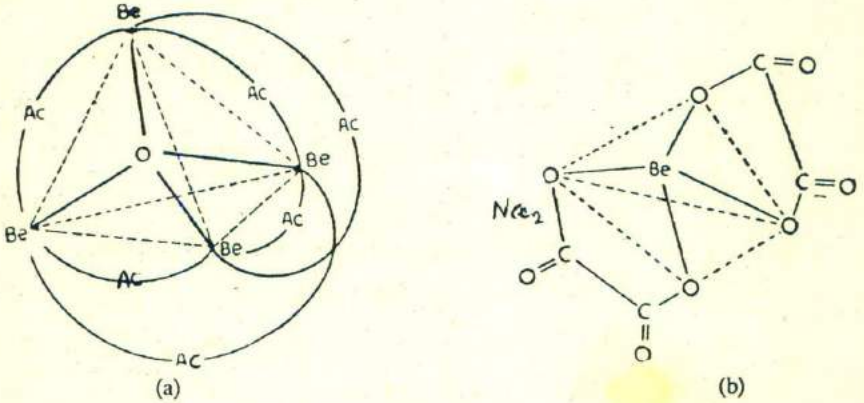


Fig. 16—2. (a) Structure of $Be_4O(CH_3COO)_6$ (Ac = CH_3COO i.e. acetate group). Be atoms at the corners of a tetrahedron. (b) Beryllium oxalate structure. Be atom at the centre of the tetrahedron.

Anomaly of Beryllium : Many properties of beryllium are in contrast to those of the other alkaline earth metals. As in the case of lithium which is a bit different from the other alkali metals and resembles with magnesium, similarly, beryllium has similar relationship with aluminium. This is in accordance with the diagonal relationship in the Periodic Table. The small size of the beryllium ion is responsible for its anomalous behaviour. Beryllium hydroxide, like $Al(OH)_3$, is amphoteric and, therefore, Be^{+2} salts are hydrolysed in water. This is not the case with other alkaline earth metal salts. Be forms quite a large number of complexes which the other alkaline earth metals do not. For instance, Na_2BeF_4 and oxalate complex, $Na_2Be(C_2O_4)_2$ etc. The interesting feature of these complexes is that beryllium is at the centre of tetrahedron and the four Be—O bonds are directed towards the corner as shown in Fig. 16—2 (b).

Be shows maximum bonds of 4 in most complexes, like Al as in $Na_2[BeF_4]$ and Al $[NH_3)_4]$ Cl_3 due to the availability of certain orbitals for bond formation. Like $Al(OH)_3$, which gives $NaAlO_2$, $Be(OH)_2$ also gives Na_2BeO_2.

Normal carbonates of Be and Al are not formed because Be and Al are weakly basic elements. The carbonates of Be and Al are extensively hydrolysed

to give basic carbonates because of their small sizes and because BeO and Al_2O_3 are much more stable than their carbonates.

Compounds of Magnesium

Magnesium oxide, MgO : This is also known as magnesia. It is obtained as follows :

(1) By burning metallic Mg in air or oxygen :

$$2Mg + O_2 = 2MgO$$

(2) By heating the hydroxide, nitrate, carbonate and even magnesite :

$$MgCO_3 = MgO + CO_2$$

$$Mg(NO_3)_2 \rightarrow MgO + NO_2$$

MgO is very light white powder and only sparingly soluble in water. It forms hydroxide very slowly. It fuses only at a very high temperature and is used for lining of furnance. MgO is used in medicine to neutralise hyperacidity. *Sorel's cement* is made by mixing fine powder of MgO with a solution of $MgCl_2$. This is a strong and durable cement and is said to be a basic salt, $MgO.MgCl_2$.

Magnesium hydroxide, $Mg(OH)_2$: This occurs as the mineral brucite. It is prepared by adding ammonia or alkali to a soluble magnesium salt :

$$MgCl_2 + 2NH_4OH = Mg(OH)_2 + 2NH_4Cl$$

A large-scale manufacture of $Mg(OH)_2$ is done by adding milk of lime to $MgCl_2$ solution.

$Mg(OH)_2$ is insoluble in water, slightly soluble on boiling but completely insoluble in ammonium chloride. The solubility of $Mg(OH)_2$ is used in qualitative analysis :

$$Mg(OH)_2 + 2NH_4Cl = MgCl_2 + 2NH_3 + 2H_2O$$

A suspension of magnesium hydroxide is called "milk of magnesia" and is used in medicine for hyperacidity of the stomach.

Magnesium carbonate, $MgCO_3$: It is found in nature as magnesite, $MgCO_3$. It is obtained as white precipitate by adding alkali carbonate solution to a solution of magnesium salt. The composition of the precipitate is

$3MgCO_3.Mg(OH)_2.3H_2O$, a basic carbonate. This is commercially known as *magnesia alba* and is used in toothpaste, cosmetic and silver polish.

$MgCO_3$ is easily decomposed by heat to MgO and CO_2. It dissolves in aqueous CO_2 to form magnesium bicarbonate, $Mg(HCO_3)_2$, which is soluble in water and is known as *fluid magnesia*. This is a constituent of hard water and the basic carbonate is precipitated from it on boiling.

Magnesium sulphate, $MgSO_4.7H_2O$: This is known as "Epsom salt". It is made by dissolving $MgCO_3$ in H_2SO_4. It is less soluble in cold water but soluble on boiling. It is used in medicine as purgative.

Magnesium chloride, $MgCl_2$: This occurs in sea water and in the mineral carnallite. It is very soluble in water and crystallizes from aqueous solution as $MgCl_2.6H_2O$. The hexhydrate is a very hygroscopic substance. When heated $MgCl_2.6H_2O$ undergoes hydrolysis and forms MgO, HCl and H_2O.

$$MgCl_2.6H_2O \rightarrow MgO + 2HCl + 5H_2O$$

On careful heating $MgCl_2.6H_2O$, the product of hydrolysis is Mg_2OCl_2 (Magnesium oxychloride) :

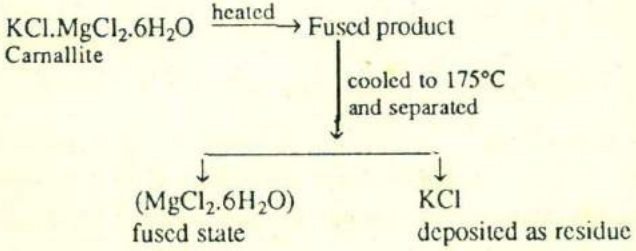
$$MgCl_2.6H_2O \rightarrow Mg_2OCl_2 + H_2O + HCl$$

Mg_2OCl_2 on strong heating gives MgO and Cl_2 :

$$2Mg_2OCl_2 + O_2 = 4MgO + 2Cl_2$$

Anhydrous $MgCl_2$: This is obtained by heating the hexahydrate in a current of hydrogen chloride or by burning magnesium in chlorine. The anhydrous $MgCl_2$ is also obtained by heating the double salt, $MgCl_2.NH_4Cl.6H_2O$. Ammonium chloride prevents the hydrolysis of $MgCl_2$ during heating. The product is fused anhydrous $MgCl_2$.

Separation of $MgCl_2.6H_2O$ from carnallite is accomplished as follows :



$MgCl_2$ in solution is used as a constituent of Sorel's cement with MgO.

Magnesium nitride, Mg_3N_2 : It is formed when magnesium is burnt in nitrogen. It s a colourless amorphous powder which is decomposed by water to $Mg(OH_2$ and NH_3. This is because Mg_3N_2 contains the true ionic species N^{-3} :

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$

Magnesium perchlorate, $Mg(ClO_4)_2$: It is obtained by dissolving $Mg(OH)_2$ in $HClO_4$:

$$Mg(OH_2 + 2HClO_4 = Mg(ClO_4)_2 + 2H_2O$$

The solution on evaporation and drying gives $Mg(ClO_4)_2$. In the anhydrous state it is a highly efficient drying agent commercially known as "*anhydrone*". It rapidly absorbs about 35% of its weight of water forming $Mg(ClO_4)_2 \cdot 6H_2O$. The drying efficiency is easily regenerated by heating the hydrate.

Magnesium phosphate : $Mg_3(PO_4)_2$ is formed when Na_3PO_4 is added to magnesium salt solution. With Na_2HPO_4 the precipitate is $MgHPO_4$.

When magnesium salt is added to a solution of phosphate in presence of ammonium chloride and ammonia, a crystalline precipitate is obtained on stirring or shaking. This is magnesium ammonium phosphate, $NgNH_4PO_4 \cdot 6H_2O$:

Dilute NH_4OH is added to neutralize H^+ ion. This is almost insoluble in water. This white substance is used for both detection and determination of either magnesium or phosphate in analytical chemistry. The estimation of magnesium or phosphate was also used to be done by burning the crystalline precipitate to magnesium pyrophosphate, $Mg_2P_2O_7$:

$$2Mg(NH_4)PO_4 = Mg_2P_2O_7 + H_2O + 2NH_3$$

Magnesium silicates : *Talc or soapstone* is a hydrated magnesium silicate, $Mg_3Si_4O_{11}.H_2O$, which is greasy to touch and soft because of layer structures. It is of commercial importance for making face powders and for household furniture.

Asbestos is a hydrated magnesium silicate, $(HO)_6Mg_6Si_4O_{11}.H_2O$, with a fibrous structure because of chain structure of silicate. It is used in making incombustible fabrics, hardboard for flooring, roofing and sheets.

The Grignard reagents: This is an important group of compounds containing magnesium carbon bond. The general formula is R—Mg—X, where R is an organic group and X is a halogen. For example, CH_3—Mg—I and C_6H_5—Mg—Br etc. These are prepared from the reaction of magnesium metal with organic halogen compound in dry ether. This is extensively used in organic synthesis.

Compounds of Calcium

Calcium oxide, CaO : This is also known as quicklime or lime. This is manufactured from limestone, $CaCO_3$, in a tall chimeny-like furance known as "limekiln", shown in Fig. 16—3.

The limestone is fed at the top of the kiln and is decomposed by hot draft of gases from below obtained by burning fuels. Sometimes a rotary kiln is also used in which the burning is done by a jet of producer gas. The CO_2 is swept away by the hot gases and thereby permits the reaction to go to completion at a lower temperature.

$$CaCO_3 = CaO + CO_2$$

Pure CaO is white amorphous powder and melts at a very high temperature, 2570°C. When strongly heated, it emits a bright light known as "limelight".

Lime is one of the most important compounds in chemical industry. It is used as a cheap alkali, for making slaked lime, bleaching powder, calcium carbide, calcium sulphite, mortar, cement and glass. It is also used in the purification of sugar and coal gas, in softening of water and tanning industries. Lime is used for liberating ammonia from ammonium salt. A mixture of CaO and NaOH is called "sodalime" and is used to remove both CO_2 and water vapour from gases.

Calcium hydroxide, $Ca(OH)_2$: When CaO reacts with water, $Ca(OH)_2$ is formed with the evolution of large amount of heat :

$$CaO + H_2O = Ca(OH)_2 + 15{,}500 \text{ cal}$$

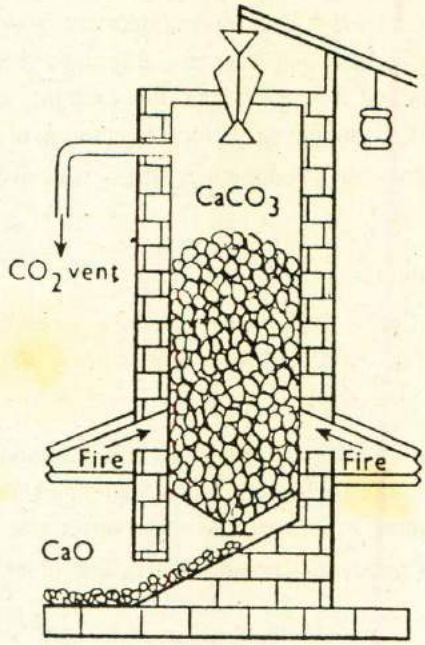


Fig. 16—3. A Lime-kiln.

Quicklime slowly exposed to the air takes up moisture and also CO_2. $Ca(OH)_2$ first formed absorbs CO_2 forming $CaCO_3$. This is the reason why lime crumbles on exposure to air.

$Ca(OH)_2$ is also known as slaked lime or hydrated lime. It is a dry white powder appreciably soluble in water. A saturated solution of $Ca(OH)_2$ is called *limewater*. A suspension of $Ca(OH)_2$ in water is known as *milk of lime*. This is used in making mortar and lime plaster for walls, ceilings and roofs because on long exposure it forms crystalline $CaCO_3$ which cements the binding materials. $Ca(OH)_2$ is used in many chemical industries mentioned in the case of lime.

Calcium carbonate, $CaCO_3$: It occurs in nature and is widely distributed as minerals known by various names, such as limestone, marble,

chalk, Iceland spar, coral etc. Precipitated chalk is obtained by passing CO_2 gas to limewater or by adding Na_2CO_3 to a solution of $CaCl_2$:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$

There are two forms of crystals of calcium carbonate : (i) Calcite and (ii) Aragonite, Calcite crystals (rhombohedra) are formed when precipitation occurs at below 33°C, while aragonite (rhombic prisms) is formed at above 30°C.

Calcite crystal is also known as "Iceland spar" and has the property of double refraction of light giving two images of the same thing. A pearl is made of $CaCO_3$ layers deposited upon a foreign particle, such as grain of sand, which has entered into the shell of an oyester.

$CaCO_3$ is not soluble in water but it dissolves in water when CO_2 is passed through the suspension forming calcium bicarbonate, $Ca(HCO_3)_2$, which is soluble in water. This solution on boiling deposits $CaCO_3$.

Cement

Cement or Portland cement is essentially powdered calcium aluminosilicate. When treated with water it sets to a hard mass resembling stone which naturally occurs in Portland, England, and hence the name Portland cement.

The raw materials for the manufacture of cement are limestone and clay. Cement is made by pulverising a mixture of limestone and clay in the proper proportions, and roasting the powder in a rotary kiln heated by gas or powdered coal to a temperature of about 1500°C. The sintered lumps obtained is called "Clinker". The clinker is mixed with about 2% gypsum, $CaSO_4.2H_2O$; and ground to a fine powder.

Limestone + clay $\xrightarrow[\text{burnt at about } 1500°C]{\text{finely powdered and}}$ Clinker $\xrightarrow{+2\% \text{ gypsum and powdered}}$ Cement

Setting of cement : The cement consists of the complex calcium aluminosilicate and it is believed that in contact with water hydrolysis occurs

forming $Ca(OH)_2$ and $Al(OH)_3$. These react with calcium silicate present forming interlocking crystals of calcium aluminosilicate and impart strengths and hardness to the mass.

Concrete is made by mixing cement with broken pieces of bricks or aggregates or stone chips together with sand. Reinforced concrete contains steel bars or netting set in the concrete.

Calcium chloride, $CaCl_2$: It is obtained as a by-product of the Solvay process for the manufacture of Na_2CO_3. This can be obtained by dissolving oxide, hydroxide or carbonate of calcium with HCl. On crystallisation, $CaCl_2.6H_2O$ is obtained. On dehydration it gives $CaCl_2$ containing a little CaO.

$CaCl_2$ is very soluble in water and with ice it forms a freezing mixture having a temperature of −55°C. The anhydrous salt is used as a drying agent for gases and liquids.

Calcium sulphate, $CaSO_4$: This occurs in nature as anhydrous $CaSO_4$ (anhydrite), and as hydrate, $CaSO_4.2H_2O$ (gypsum). The crystalline form of $CaSO_4.2H_2O$ is called *alabaster*. Calcium sulphate is obtained in the form of precipitate when $Ca(NO_3)_2$ is treated with Na_2SO_4 or dil H_2SO_4.

On heating gypsum, it loses water and forms $(CaSO_4)_2.H_2O$:

$$2\,CaSO_4.4H_2O \xrightarrow[120°C]{heat} 2CaSO_4.H_2O + 3\,H_2O$$

The hemihydrate, $2CaSO_4.H_2O$, is known as "Plaster of Pairs." When ground to fine powder and mixed with water to form a paste, it sets to a hard mass forming small interlocking crystals of gypsum, $CaSO_4.2H_2O$. The anhydrous $CaSO_4$ does not possess the property of setting with water. Plaster of Paris is used in making plaster casts, moulds and for building purposes.

Calcium sulphide, CaS : It is made by several processes, such as when lime is heated in H_2S gas or when $CaSO_4$ is reduced with C :

$$Ca(OH)_2 + H_2S \xrightarrow{heat} CaS + 2\,H_2O$$

$$CaSO_4 + C \xrightarrow{heat} CaS + 2\,H_2O$$

It is a white powder and has a remarkable phosphorescence due to the presence of trace impurities, such as Bi, Mn, Cu etc. CaS is hydrolysed in H_2O to give $Ca(HS)_2$:

$$CaS + 2H_2O = Ca(OH)_2 + Ca(HS)_2$$

CaS and $Ca(HS)_2$ are used for removing hairs from skins and in tanning industries for removing hair from hides.

Calcium oxalate, CaC_2O_4 : When ammonium oxalate solution is added to a neutral Ca-salt solution in the hot condition, a white precipitate is obtained which is $CaC_2O_4.H_2O$, but insoluble in acetic acid and alkalis. The precipitation of CaC_2O_4 is used in the detection and estimation of Ca both gravimetrically by ignition to CaO and volumetrically by dissolving the precipitate in dil H_2SO_4 and titrating the liberated oxalic acid with $KMnO_4$ solution.

[For CaC_2 and $CaCN_2$ see Chapter 19 and for bleaching powder see Chapter 22]

Compounds of Strontium

Strontium oxide, SrO : This is obtained by a similar method as CaO, i.e. by heating of $SrCO_3$ or $Sr(NO_3)_2$:

$$SrCO_3 = SrO + CO_2$$

$SrSO_4$ (celstine mineral) is converted to SrO by reducing $SrSO_4$ to SrS by C and treating with NaOH :

$$SrSO_4 + 2C = SrS + 2CO_2$$

$$SrS + 2NaOH = Na_2S + Sr(OH)_2$$

$Sr(OH)_2$ being less soluble is freed from Na_2S by water. $Sr(OH)_2$ on strong heating gives SrO.

SrO is slaked, like lime, with H_2O forming $Sr(OH)_2$ and has been used for the recovery of sugar from molasses by the process known as "Strontia method".

All other compounds of Sr are obtained by similar reactions as described in the case of Ca compounds.

Compounds of Barium

Barium oxide, BaO : This is produced by heating $BaCO_3$ with finely divided carbon. The purpose of adding carbon is to reduce CO_2 to CO and thus to shift the equilibrium $BaCO_3 \rightleftharpoons BaO + CO_2$ to the right direction. The conversion of carbonate to BaO takes place at a much lower temperature than the decomposition temperature of $BaCO_3$. BaO is also made from $Ba(NO_3)_2$ which easily decomposes when heated :

$$BaCO_3 + C = BaO + 2CO$$

$$2\,Ba(NO_3)_2 = 2\,BaO + 2NO_2 + O_2$$

BaO is a white powder and is known as *Baryta* It reacts with water to form $Ba(OH)_2$. $Ba(OH)_2$. is more soluble in water than $Ca(OH)_2$ or $Sr(OH)_2$ whereas $Mg(OH)_2$ and $Be(OH)_2$ are least soluble. The solution of $Ba(OH)_2$ in water is known as *Baryta water*. It appears that the strength of the crystal forces decreases with increasing cation sizes. $Be(OH)_2$ has the largest lattice energy and hence it is not easily soluble and so is the case with BeO. The lattice energies of the hydroxides and oxides of the alkaline earth metal decrease form Be to Ba.

BaO is used for the preparation of BaO_2. This is more easily formed than the preoxide of Ca or Sr. BaO_2 is obtained on heating BaO in air or oxygen at about 500°C :

$$2BaO + O_2 \rightleftharpoons 2BaO_2$$

On heating BaO_2 to about 700°C, it is decomposed giving BaO and oxygen. BaO_2 has been used for the production of H_2O_2 according to the reaction :

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$

Barium sulphate, $BaSO_4$: It occurs in mineral "Barytes", $BaSO_4$. It is obtained by adding a soluble sulphate to a barium-salt solution :

$$Na_2SO_4 + BaCl_2 = BaSO_4 + 2\,NaCl$$

$BaSO_4$ is insoluble in water but slightly soluble in conc HCl and conc H_2SO_4. The larger hydration energy of large SO_4^{-2} and Ba^{+2} ion makes $BaSO_4$ insoluble. smaller sizes of Be^{+2} and Mg^{+2} impart lower hydration energies for $BeSO_4$ and $MgSO_4$ which are soluble in water.

$BaSO_4$ is a starting material for all other barium compounds. $BaSO_4$ is converted into $BaCO_3$ by heating with Na_2CO_3 either in the solid state or in solution :

$$BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$$

It is also converted into BaS by reduction with carbonate at high temperature :

$$BaSO_4 + 4C = BaS + 4CO$$

BaS or $BaCO_3$ may then be dissolved in acids to produce the desired salts. The formation of insoluble $BaSO_4$ is used for identification and determination of both barium and sulphate.

Barium sulphide, BaS : It is made as mentioned above. It is a white powder and is decomposed by water forming $Ba(OH)_2$ and liberating H_2S.

It is used for removing hair form skins and hides. BaS is mixed with $ZnSO_4$ in aqueous solution to give a white precipitate consisting of a mixture of $BaSO_4$ and ZnS. This is isolated and dried in the powder form which is known as *"Lithopone"* :

$$BaS + ZnSO_4 = BaSO_4 + ZnS$$

Lithopone is not darkened by H_2S unlike white lead.

Barium chromate : This is obtained in the form of lemon-yellow insoluble precipitate when a soluble chromate is added to barium salt solution :

$$BaCl_2 + K_2CrO_4 = 2KCl + BaCrO_4$$

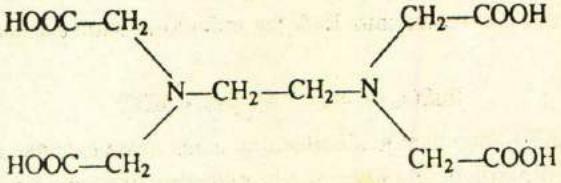
Ca and Sr do not form insoluble chromates and hence the precipitate of $BaCrO_4$ is used as a distinguishing test for Ba.

[N. B. The chemistry of radium which is almost similar to that of other alkaline earth metals, particularly to that of Ba has been described in chapter 27.]

Complex Compounds of Alkaline Earth Metals

Like the alkali metals, the alkaline earth metals are not very versatile in forming complex compounds. The complex forming ability decreases with the increase in atomic number in this group because of the increase in the size of the ions. But when an ion is encircled by a cyclic structure, it gives rise to a

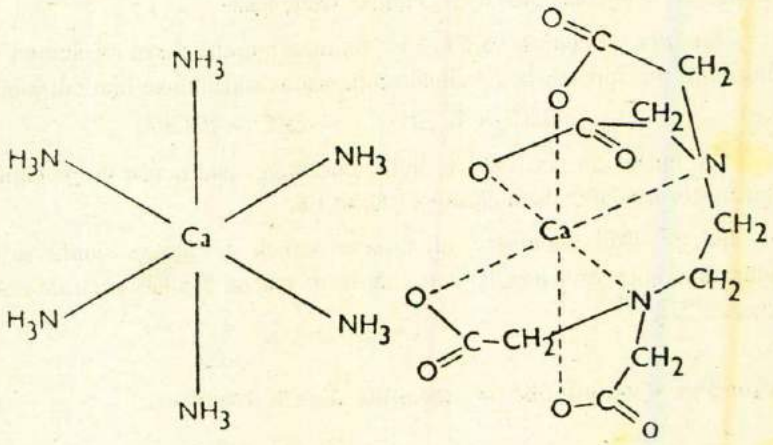
complex of great stability. Thus, $CaCl_2.6NH_3$ is a very unstable complex and NH_3 is readily given off, but Ca^{+2} forms a stable complex with EDTA (ethylence diamine tetra-acetic acid), the anion of which completely envelops Ca^{+2} ion as shown in shown in Fig. 16—4.



Ethylene diamine tetra-acetic acid

Mg^{+2} forms quite stable complexes of the cyclic structure types as the naturally occuring "chlorophyll" in which Mg is surrounded by four nitrogen forming part of a large organic ring called "porphyrin" group.

Be complexes have been mentioned earlier. Other alkaline earth metals are not important complex-forming elements.



$6NH_3$ in $CaCl_2$ (open structures)

Ca-EDTA complex (with Na_2EDTA) (cyclic structure)

Fig. 16—4. Structures of $Ca(NH_3)_6^{+2}$ and $[Ca\text{-}EDTA]^{-2}$ complex

QUESTIONS AND PROBLEMS

1. Write short notes on alkaline earth metals and their compounds.
2. Describe the preparation and properties of the following and mention some of their uses :—

   (a) Calcium cyanamide, (b) Lithopone.
3. How will you detect Ca and Ba in a solution ?
4. (a) what is carnallite ? How this can be used to obtain magnesia ?

   (b) Described briefly the electrometallurgy of magnesium using magnesia as the raw materials.

   (c) Mention some of the properties and uses of magnesium.
5. Describe the preparation and properties of calcium carbide
6. Discuss the anomalies in the chemistry of lithium and compare it with that of magnesium.
7. Write a note on the manufacture of Portland cement.
8. What is Portland cement? How does it differ from glass ? Describe briefly the manufacture of Portland cement from the raw-meterials available in Bangladesh laying special emphasis on the chemical reactions occurring in the rotary kiln.
9. How will you justify the inclusion of alkaline earths in the same group of periodic chart ? How do they compare with Zn, Cd and Hg ?
10. Describe the preparation and properties of magnesium.
11. Describe the preparation and uses of anhydrous magnesium chloride.
12. Show the distribution of electrons in the atoms of Be (4), Mg (12) and Ca (20). Explain the similarities in chemical properties of Be, Mg and Ca with reference to the arrangement of orbital electrons.
13. Write a short note on the gradation of properties in alkaline earth metals.
14. Discuss the anomalous position of Be with the alkaline earth metals. In what respects Be is different from other alkaline earth metals and why ?
15. Describe briefly the electrometallurgy of Mg.
16. Explain the dissolution of magnesium salts in NH_4Cl.
17. It is not possible to prepare anhydrous $MgCl_2$ by heating $MgCl_2.6H_2O$. Why ?
18. What are the essential reactions involved in the setting of cement ?
19. Compare the chemistry of lithium and magnesium.
20. Write short notes on :
    Alkaline earth metals and their compounds.

21. Discuss the two methods of preparation of beryllium from beryl. Compare the properties of beryllium with those of aluminium.
22. Write short note on "lithopone".
23. Give a description of the preparation and uses of quicklime.
24. Write the reactions of Ca^{+2} with the following : (a) HCO_3^- (b) Soap anion $CH_3(CH_2)_{16}COO^-$ (c) Na_2Ze (Ze = Zeolite) (d) anion exchange resin ($R\text{-}SO_3^-$).
25. What happens when CaC_2 and Mg react with atmospheric nitrogen when heated in air.
26. Write the chemical reaction for the preparation of magnesium from sea water. What are other elements which can be isolated from sea water.
27. What are the unique properties of $CaSO_4.2H_2O$, $CaSO_4.0.5H_2O$ and $Ca(HSO_3)_2$?
28. Some solid CaO in a test tube picks up water vapour from air and completely changed to $Ca(OH)_2$. The weight of the test tube with CaO was 10.860 g which increased to 11.149 g. What is the weight of the test tube ?

CHAPTER 17
ZINC, CADMIUM AND MERCURY

(Elements of Group IIB)

The metals of group IIB bear the same relation to the alkaline earth metals as those of group IB do to the alkali metals. Each of the metals Zn, Cd and Hg has two electrons in the outermost level immediately after the completed d^{10} level. The outer two valence electrons of these metals determine their chemistry.

The Electronic Structure : The electronic structures of Zn, Cd and Hg are given in Table 17.1.

Table 17.1. Electronic structures of Group IIB

At. No.	*Elements*	*Electronic Configuration*	*Valence electrons*
30	Zn	Ar core, $3d^{10}4s^2$	$4s^2$
48	Cd	Kr core, $4d^{10}5s^2$	$5s^2$
80	Hg	Xe core, $4f^{14}5d^{10}6s^2$	$6s^2$

Thus, it can be seen that there are two electrons (s^2) in each of the metals in the outermost orbitals.

Comparative Chemistry of Zn, Cd and Hg

It is expected that the two s electrons beyond the d^{10} sub-level will be lost giving the oxidation state of +2 in each case which is generally observed. But in the case of Hg it forms a univalent ion, Hg_2^{+2}, in some of its compounds although generally it is Hg^{+2}. Univalent Cd and Zn are not formed. Moreover, Hg is less reactive than the other two and occurs in the "free state" in nature indicating the $6s^2$ electrons to be not very active and thus resemble with its neighbour Au. The electron configuration of $5d^{10}6s^2$ in Hg is an stable arrangement. The $6s^2$ electrons become almost inert. The formation of

monoatomic Hg in vapour state, small degree of ionization of $HgCl_2$ and formation of mercurous salt of Hg_2Cl_2 type indicate inertness of $6s^2$ electrons.This is not so well-marked in the case of Zn and Cd. The physical properties of Zn, Cd and Hg are given in Table 17.2.

Table 17.2 Physical properties of Zn, Cd and Hg.

Properties	*Zn*	*Cd*	*Hg*
At. No.	30	48	80
At. wt.	65.38	112.41	200.61
Outer electron orbitals	$3d^{10}4s^2$	$4d^{10}5s^2$	$5d^{10}6s^2$
Atomic radius (Å)	1.33	1.49	1.50
Ionic radius (Å)	0.74	0.97	1.10
Ionization potential (ev)	9.39	8.99	10.43
Electronegativity	1.66	1.46	1.44
Density at 20°C (g/cm^3)	7.14	8.6	13.55
Melting point (°C)	419	320	–39
Boiling point (°C)	907	767	357
Oxidation potential (v)	$Zn/Zn^{+2} + 0.76$	$Cd/Cd^{+2} + 0.40$	$Hg/Hg_2^{+2} - 0.79$
			$Hg/Hg^{+2} - 0.85$
Oxidation states	+2	+2	+1, +2
Vaporization energy Kcal/mole at 25°C	31.2	27.0	14.5

It is seen that the melting points, boiling points and heats of vaporization of Zn, Cd and Hg are lower than any group of elements (except IA). The atoms of Zn, Cd and Hg, because of larger sizes, have small interatomic attractions. Hence they have low melting and boiling points. Hg has very weak interatomic forces and melts below room temperature. It is expected that these metals should have high oxidation potentials. The metals Zn and Cd are, therefore, easily oxidized but Hg is less susceptible to oxidation. The properties of these metals show the effect of the higher ionization potentials and the small size of the respective ions.

Some of the properties which are similar may be enumerated as follows :—

Similarities : 1. All the three metals form bivalent ions, M^{+2}.

2. They do not form any hydrides.

3. They are readily reduced to the metallic state from their ores and compounds. This is the reason that the metallic Zn and Hg are known from the earliest time.

4. Like coinage metals, these metals also form a large number of complexes and volatile organometallic compounds.

Dissimilarities : There are some irregularities in the gradation of properties within this group. These are :—

1. Zn and Cd are similar to each other and are different from mercury. Hg has very low melting point.

2. As the atomic number increases, the oxides (MO) become less stable towards heat. The chlorides (MCl_2) become less easily hydrolysed and the sulphides (MS) become more deeply coloured and less soluble in water.

ZnS is white and soluble in dil HCl. CdS is yellow-orange and soluble in conc HCl. HgS may be black and dissolves only in aqua regia.

3. HgO is the most basic and ZnO is amphoteric in the group Zn, Cd and Hg. This is in line with the increase in ionic radius from Zn to Hg.

4. $ZnCl_2$ is hygroscopic and dissolves readily to form Zn^{+2}. $CdCl_2$ gives ions of the type $CdCl^+$, $CdCl_3^-$ and $CdCl_4^{-2}$. $HgCl_2$ is practically non-ionised in aqueous solution. $HgBr_2$ and HgI_2 are almost insoluble in water.

5. $Zn(OH)_2$, $Cd(OH)_2$ and $Hg(OH)_2$ are unstable, particularly $Hg(OH)_2$, which is not formed. The structure of the positive ions having non-inert gas structure are less stable.

6. Zn and Cd readily dissolve in acids giving hydrogen. Hg does not liberate hydrogen from acids. Hg, in fact, is a "noble metal." The electrophilic tendency of Zn due to the still less shielded 3d electrons and its ionic size makes it similar in properties to Be^{+2} and Al^{+3}.

Occurrence : Zn and Cd occur together in minerals, such as ZnS and $ZnCO_3$. Hg is found in the free state or as sulphide ore, HgS.

The Comparison of Group IIA and IIB Metals

Although Zn, Cd and Hg have been placed in group II along with the alkaline earth metals and have some well-marked similarities, as in the formation of dipositive ions, there are many points of contrast. They are widely separated in the Periodic Table by the transition elements. These arise mainly because the electron configurations of IIA and IIB do not have the same penultimate orbitals. Thus the alkaline earth elements have s^2 electrons after an inert gas configuration whereas Zn, Cd, Hg have s^2 electrons after the completion of the transition series of d^{10} electrons.

1. Group IIA metals are light and have high atomic volume and atomic radii. Group IIB are heavier and have smaller size. The two s electrons in the two sub-groups in the outermost orbitals are not similar in arrangement.

2. Group IIA metals have high melting points whereas group IIB metals have low melting points. Hg is liquid at ordinary temperature (melting point $-39°C$).

3. Group IIA metals are reactive because the two s electrons occur just after the s^2p^6 orbitals of an inert gas electron arrangement. Group IIB metals are quite stable. The former are easily attacked by atmospheric action but IIB are not readily attacked.

4. Oxides of group IIA cannot be easily reduced to metals whereas group IIB metals can be easily reduced to the respective metals with carbon or by simple heating as in the case of HgO. The ionic character of group IIA compounds is more pronounced than that of the IIB compounds.

5. Group IIA generally forms colourless compounds, IIB forms quite a large number of coloured compounds, particularly Hg, because it is easy to excite electrons of the d orbitals by polarisation as in the case of HgI_2.

6. Group IIA sulphates are insoluble in water whereas group IIB sulphates are soluble.

7. Group IIB metals form complex compounds with ammonia, IIA does not.

Metallurgy of Zn, Cd and Hg

Extraction of Zinc : Zinc is extracted from its ores by (i) carbon reduction process or (ii) electrolytic process.

Sources :

Zinc blende—ZnS

Zincite— ZnO

Calamine— $ZnCO_3$

1. Carbon reduction process : The following metallurgical steps are involved in the extraction of Zn by carbon reduction process :—

(a) The ground ore is concentrated by froth floatation process.

(b) The concentrated ore is roasted to convert it into oxide :

$$2ZnS + 3O_2 = 2ZnO + 2SO_2$$

Some $ZnSO_4$ formed is also decomposed to ZnO :

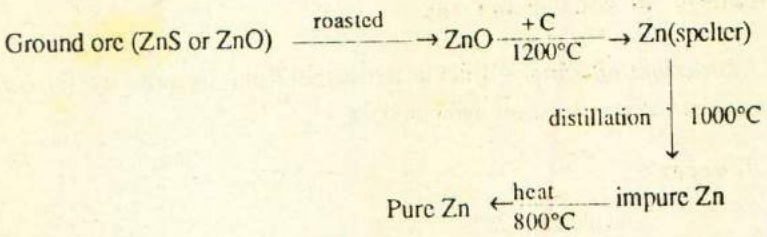
$$2ZnSO_4 = 2ZnO + 2SO_2 + O_2$$

(c) The oxide is heated with carbon in retorts. ZnO is reduced to Zn and is distilled :

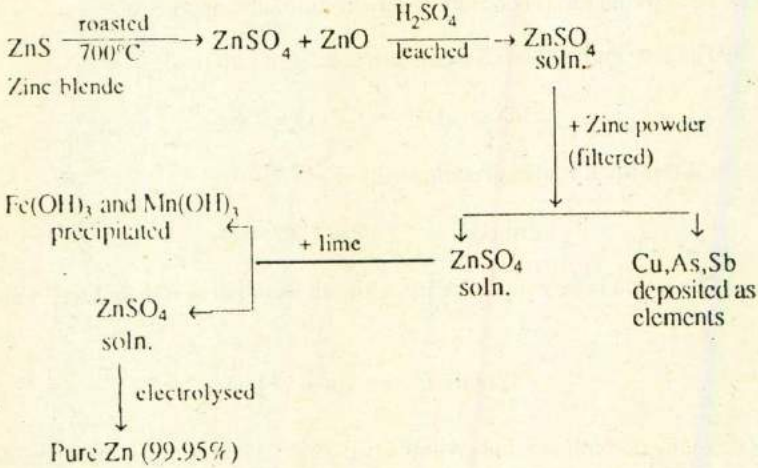
$$ZnO + C = Zn + CO$$

Zn obtained is impure and contains Cd. The reduction of ZnO is carried out in various types of furnaces, such as retort furnace, reverberatory furnace and vertical furnace which have different designs to collect the molten Zn in the form of condensate.

Purification of impure Zn : Zn obtained by the carbon reduction process is impure and is called "spelter". This is distilled at about 1000°C when only Zn and Cd are distilled over. Zn is made free from Cd by heating at about 800°C at which temperature only Cd is distilled over :



2. Electrolytic process: In this process the ore is roasted in a special furnace under controlled conditions to convert the sulphide to sulphate. The roasted ore is leached with dilute H_2SO_4 to dissolve $ZnSO_4$ and sulphates of other metals. The purified solution is electrolysed with aluminium cathode. Pure Zn deposits on the cathode and is scrapped off :



Extraction of Mercury :

Sources : Cinnabar — HgS

Extraction : The metallic mercury is produced by roasting cinnabar. Sulphur is removed as sulphurdioxide and mercury distils from the furnace and is condensed to the liquid :

$$HgS + O_2 = Hg + SO_2$$

The roasting of HgS in air gives some amount of HgO, but HgO is thermally unstable and decomposes readily at high temperature. The roasting of HgS is done in different types of furnaces, such as reverberatory furnace, muffle furnace or shaft furnace with arrangement of collecting distilled metallic mercury.

Metallic mercury is purified by filtering through chamois leather, washing it with nitric acid or by distillation in presence of oxygen.

Uses of Zn, Cd and Hg

Zn : Zn is used in the manufacture of dry cells and in the production of alloys, such as brass and bronze (see copper). Large quantity of Zn is used to protect iron and other metals from corrosion by air and water. The protective action of Zn is based upon the fact that a film of basic zinc carbonate is formed on the surface.

Zinc coating on iron is applied by various methods and the product is known as "galvanized iron". Galvanizing is done by various methods.

(a) Hot galvanizing : Iron or steel is first thoroughly cleaned by washing with caustic soda and by "pickling" in dilute H_2SO_4. The cleaned iron is then dipped into molten zinc bath. The hot galvanized iron piece forms an alloy of iron and zinc on the surface with a layer of pure zinc outside.

(b) Electro-galvanizing : This is also known as cold galvanizing. This involves the continuous passage of iron strips of wires through a plating bath. Zn of high purity is deposited on the surface by this process.

(c) Sherardizing : In this process a layer of Zn is applied to small iron objects by placing them in a revolving drum with zinc dust, and heating to a high temperature to form zinc-iron alloy on the surface.

(d) Metallising process : In this process the iron object is coated by spraying atomised zinc against the iron with great force. The layer of Zn adheres to the iron surface.

Cd : Cadmium metal is used as control rods for neutron captures in atomic reactors. It is used in Weston Standard Cell. Large number of alloys of cadmium are made for special use.

Hg : Mercury is used as an excellent thermometric and barometric substance. All metals (except Fe and Pt) dissolve in mercury or form *amalgams* which are used for various purposes, e. g., as reducing agent (Na—Hg), dentistry (Ag—Hg) etc. Mercury vapour lamps and fluorescent lamps are used for lighting highways because mercury in vapour condition is a good conductor of electricity and in doing so emits brilliant light.

Some Important Compounds of Zn, Cd and Hg

Compounds of Zinc

Zinc oxide, ZnO : This is obtained by burning zinc vapour in air. It is also prepared by precipitating basic zinc carbonate from zinc sulphate and then heating the precipitate to form ZnO.

It is a white powder which becomes yellow on heating. The white colour reappears on cooling. ZnO dissolves in acids producing zinc salt and in alkalis it gives zincates because of its amphoteric character:

$$ZnO + 2NaOH = Na_2ZnO_2 + H_2O$$

The white ZnO, commercially known as "zinc white", is used as pigment and also in the preparation of *"Rinman's Green"* which is also a pigment obtained by heating ZnO with a solution of $Co(NO_3)_2$ and has the composition $CoZnO_2$ (cobalt zincate). This is also formed during the blow-pipe test for zinc.

Zinc hydroxide, $Zn(OH)_2$: It is obtained as a white flocculent prepitate on adding alkali to a solution of zinc salt. The precipitate is insoluble in water but readily dissolves in excess of alkali forming zincate in solution :

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$$

$$Zn(OH)_2 \rightleftharpoons Zn^{+2} + 2OH^-$$

$$Zn(OH)_2 + 2OH^- \rightleftharpoons Zn(OH)_4^{-2}$$

In is dissolved in excess of ammonia to give a complex hydroxide :

$$Zn(OH)_2 + 4NH_4OH = Zn(NH_3)_4(OH)_2 \rightleftharpoons [Zn(NH_3)_4]^{+2} + 2OH^-$$

Zinc carbonate, $ZnCO_3$: It is formed when :

(1) Zn or ZnO dissolves in water in presence of CO_2 :

$$Zn + H_2O + CO_2 = ZnCO_3 + H_2$$

$$ZnO + H_2O + CO_2 = ZnCO_3 + H_2O$$

(2) Basic zinc carbonate is precipitate by adding sodium carbonate to a solution of zinc salt but on boiling it is converted to ZnO :

$$ZnCl_2 + Na_2CO_3 = ZnCO_3.Zn(OH)_2 \xrightarrow[\text{boiled}]{+\,Na_2CO_3} ZnO$$

$ZnCO_3$ decomposes at about 160°C :

$$ZnCO_3 = ZnO + CO_2$$

Zine sulphate, $ZnSO_4.7H_2O$: It is known as *white vitriol* and is very soluble in water. It is obtained by dissolving Zn, ZnO or $ZnCO_3$ in dilute H_2SO_4, evaporating the solution and crystallising to give crystals of $ZnSO_4.7H_2O$.

On heating $ZnSO_4.7H_2O$ at about 300°C it is converted to anhydrous $ZnSO_4$. At about 750°C it is decomposed to ZnO and SO_3 :

$$ZnSO_4 = ZnO + SO_3$$

It is used for making a white paint known as "lithopone".

Zinc chloride, $ZnCl_2$: Anhydrous $ZnCl_2$ is formed by passing Cl_2 gas over Zn or by distilling Zn with $HgCl_2$ because $ZnCl_2$ sublimes at a lower temperature than $HgCl_2$:

$$Zn + Cl_2 = ZnCl_2$$

$$Zn + HgCl_2 = ZnCl_2 + Hg$$

It can be made from ZnO or $ZnCO_3$ by the action of conc HCl, evaporating the solution to dryness and fusing the residue to remove moisture. The white product melts at 262°C and is cast into sticks. Dilute HCl gives Zn(OH)Cl and Zn_2OCl_2.

$ZnCl_2$ is very deliquescent and extremely soluble in water, alcohol, ether, acetone etc. Concentrated solution of $ZnCl_2$ dissolves cellulose which can be moulded like plastic. $ZnCl_2$ solution is used as wood preservative. Zn_2OCl_2 with water sets to a hard mass. These zinc compounds are very toxic and should be handled with care.

Zinc sulphide, ZnS : It occurs in nature as zinc blende, ZnS. When H_2S is passed into a Zn-salt solution in presence of NH_4OH and NH_4Cl, the white precipitate of ZnS is obtained. This is soluble in HCl but insoluble in acetic acid. ZnS can also be precipitated from $ZnSO_4$ solutions containing sodium acetate by passing H_2S :

$$ZnSO_4 + H_2S + 2NH_4OH = ZnS + (NH_4)_2SO_4 + 2H_2O$$

ZnS is used as a white pigment. ZnS containing traces of impurities such as Mn, Ca, Bi, Pb etc., is phosphorescent and can be used for luminous paints.

Zinc ethyl, $Zn(C_2H_5)_2$: This is made by heating Zn metal with ethyl iodide. This is an inflammable volatile liquid :

$$Zn + 2C_2H_5I = Zn(C_2H_5)_2 + I_2$$

This is used for making zinc amide, $Zn(NH_2)_2$ and ZnH_2 which cannot be made directly :

$$Zn(C_2H_5)_2 + 2NH_3 = Zn(NH_2)_2 + 2C_2H_6$$

$$Zn(C_2H_5)_2 + LiAlH_4 = ZnH_2 + LiAlH_2(C_2H_5)_2$$

$Zn(NH_2)_2$ on heating to redness gives Zn_3N_2 :

$$3Zn(NH_2)_2 = Zn_3N_2 + 4NH_3$$

Compounds of Cadmium

Cadmium is isolated during the purification of zinc. Cadmium is more volatile than zinc and is distilled off.

The compounds of cadmium have similar properties as those of zinc. CdO and $Cd(OH)_2$ do not show amphoteric character as ZnO and $Zn(OH)_2$. $Cd(OH)_2$ is not soluble in NaOH.

Cadmium sulphide, CdS : It is formed when H_2S is passed through a solution of Cd-salt in neutral, alkaline or feebly acidic medium. It is generally yellow-orange in colour unlike ZnS which is white. CdS is not precipitated by H_2S if acid concentration is high. CdS is soluble in KI solution forming a complex K_2CdI_4.

Cadmium sulphate, $CdSO_4.8H_2O$: When CdO is dissolved in dilute H_2SO_4 it forms $CdSO_4$ in solution which on evaporation gives $CdSO_4.8H_2O$. $CdSO_4$ is used in "Weston Standard Cell" which has Cd—Hg and Hg electrodes

containing $CdSO_4$ and mercurous sulphate. The E. M. F. is 1.019 volts at 20°C. The E. M. F. remains constant because the solubility of $CdSO_4$ does not vary with temperature.

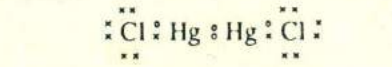
Cadmium chloride, $CdCl_2$: It is not deliquescent nor hydrolysed with water like $ZnCl_2$. The crystals lose water of crystallisation if any.

Cadmium cyanide, $Cd(CN)_2$: It is formed when KCN is added to a solution of Cd-salts. The precipitate dissolves in excess KCN forming a complex $K_2Cd(CN)_4$ which gives CdS on passing H_2S. Copper is not precipitated as CuS from $K_2Cu(CN)_4$ solution and this fact is used for the separation of Cu from Cd.

Compounds of Mercury

Mercury forms two types of compounds containing mercurous, Hg^{+} and mercuric, Hg^{+2}. Some of the important compounds of both are described here.

Compounds of univalent mercury : The mercurous ion is a peculiar ion having Hg—Hg bond. The univalent mercury has been proved to be a dimer by various methods. Thus, the determination of molecular weight by vapour density or cryoscopic methods, X-ray studies of mercurous chloride and spectral studies show the presence of Hg_2^{+2} rather than Hg^{+}. The compounds of Hg_2^{+2} are diamagnetic and hence cannot contain the monomer Hg^{+2} ion. The ease with which metallic Hg is liberated from mercurous compounds also points to the formation of Hg : Hg^{+2} ion. One valence electron of each Hg in mercurous compounds forms an electron-pair bond with the second Hg atom. Hg_2Cl_2 is thus :



Metallic Hg is easily released from Hg^{+1}, i. e. Hg_2^{+2} compounds. Thus,

$$Hg_2S = HgS + Hg \text{ (heat)}$$

$$Hg_2Cl_2 + H_2O = HgCl_2 + Hg \text{ (boiled)}$$

$$Hg_2O = HgO + Hg \text{ (heat)}$$

The study of the equilibrium between liquid Hg, Hg^{+2} ion and Hg_2^{+2} ion supports the formulation of Hg_2^{+2} ion for the mercurous mercury. Thus for

$Hg + Hg^{+2} \rightleftharpoons Hg_2^{+2}$, $K = [Hg_2^{+2}] / [Hg^{+2}]$ has been found to be valid since the value of K is constant. The other possibility :

$$Hg + Hg^{+2} \rightleftharpoons 2Hg^{+}$$

gives the constant, $K' = [Hg^+]^2/[Hg^{+2}]$ which is not valid since K′ does not give constant value indicating absence of Hg^+ ion.

Mercurous ions do not normally form any complex. Hg_2Cl_2 is not soluble in ammonia (compare from Ag^+).

Mercurous chloride (calomel), Hg_2Cl_2 : This is commercially made by heating a mixture of $HgSO_4$, Hg and NaCl :

$$HgSO_4 + Hg + 2NaCl = Hg_2Cl_2 + Na_2SO_4$$

Also by the reaction :

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$

Hg_2Cl_2 is volatile and sublimes off in the form of white powder from the reaction mixture. It is insoluble in water and in dilute HCl which precipitates Hg_2^{+2} as Hg_2Cl_2 in group I of chemical analysis.

Hg_2Cl_2 decomposes to $HgCl_2$ and Hg on exposure to light and it is stored in brown bottles :

$$Hg_2Cl_2 = HgCl_2 + Hg$$

Hg_2Cl_2 with $SnCl_2$ is reduced to Hg :

$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4$$

Hg_2Cl_2 in generally known as *Calomel* and is used as medicine and in calomel electrode.

Mercurous nitrate, $Hg_2(NO_3)_2$: When mercury is dissolved in dilute HNO_3, the product is $Hg_2(NO_3)_2$ in presence of excess of Hg. It is the only readily soluble salt of mercurous Hg. The compound is hydrolysed in aqueous solution forming $Hg_2(OH)NO_3$:

$$2Hg + 2HNO_3 = Hg_2(NO_3)_2 + H_2$$
$$Hg_2(NO_3)_2 + H_2O \rightleftharpoons Hg_2(OH)NO_3 + HNO_3$$

$Hg_2(NO_3)_2$ is readily oxidized to $Hg(NO_3)_2$.

Mercurous oxide, Hg_2O : When NaOH solution is added to a solution of $Hg_2(NO_3)_2$, a dark brown powder is precipitated which is Hg_2O. This is decomposed in light to give HgO + Hg.

Mercurous sulphide, Hg_2S : When H_2S is passed into a solution of $Hg_2(NO_3)_2$, a precipitate of Hg_2S is formed which instantaneously changes into HgS :

$$Hg_2(NO_3)_2 + H_2S = Hg_2S + 2HNO_3$$
$$\downarrow$$
$$HgS + Hg$$

Mercurous iodide, Hg_2I_2 : It is obtained by means of intimately mixing HgI_2 with I_2 forming a green powder and is changed to HgI_2 by simple heating.

Mercurous sulphate, Hg_2SO_4 : On heating Hg with conc H_2SO_4 both Hg_2SO_4 and $HgSO_4$ are formed. When H_2SO_4 is added to $Hg_2(NO_3)_2$, white precipitate of Hg_2SO_4 is obtained. This is hydrolysed in hot water :

$$2Hg_2SO_4 + H_2O = (Hg_2)_2OSO_4 + H_2SO_4.$$
$$\downarrow$$
$$Hg_2OSO_4 + 2Hg$$

Compounds of divalent mercury (Hg^{+2}) : The mercuric ion forms mostly covalent compounds. The strong oxyacids, such as H_2SO_4, HNO_3 and $HClO_4$, form ionic compounds with mercury which dissociate in aqueous solution. The bonds between Hg and S, C, Cl, Br or I etc. are covalent. The energies involved in the covalent bond formation with Hg are small but the bonds are stable towards air, water, acids and alkalis indicating strong covalent bond.

Mercuric oxide, HgO : When a strong alkali is added to a solution of Hg salts, HgO is precipitated. In the cold, the precipitate of HgO is yellow but from hot solution it is red. This difference is due to the fine state of sub-division of HgO. Both the varieties of HgO have the same crystal structures.

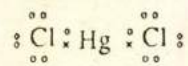
The formation of $Hg(OH)_2$ does not take place since it is unstable and is decomposed to HgO and H_2O. The red HgO is also made by adding hot solutions of $HgCl_2$ and K_2CO_3 :

$$HgCl_2 + K_2CO_3 = HgO + 2KCl + CO_2$$

Mercuric chloride, $HgCl_2$: It is obtained by heating Hg in an excess of chlorine or by dissolving HgO in HCl or in aqua regia. Commercially it is made from $HgSO_4$ and NaCl by heating :

$$2NaCl + HgSO_4 = Na_2SO_4 + HgCl_2$$

$HgCl_2$ is known as *corrosive sublimate* because of its corrosive properties and is a strong poison. It is soluble in many organic solvents and moderately soluble in water but only slightly ionized $HgCl_2$ has the formula,



The structure of $HgCl_2$ uses sp hybrid orbitals of Hg as in the case of Be compounds and is a linear molecule :

$$Cl—Hg—Cl$$

$HgCl_2$ dissolves in solution containing chloride ion to form stable complexes of the type $HgCl_4^{-2}$:

$$HgCl_2 + 2Cl^- \rightleftharpoons HgCl_4^{-2}$$

Mercuric chloride is ammonolysed to give ammonobasic mercuric chloride :

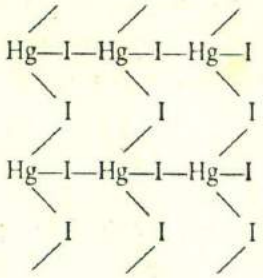
$$Cl—Hg—Cl + 2NH_3 \rightarrow Cl—Hg—NH_2 + NH_4^+ + Cl^-$$

With $SnCl_2$, Hg_2Cl_2 is precipitated :

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$

Mercuric iodide, HgI_2 : When potassium iodide is added to a solution of $HgCl_2$, a red precipitate of HgI_2 is formed. This is soluble in excess of KI and also in excess of $HgCl_2$ forming complexes.

HgI_2 like other mercuric halides is linear in the solid state and is linked together in layer structure. HgI_2 has simple layer structure :



The formation of the complexes of HgI_2 is given by the equation :

$$HgI_2 + 2KI = K_2HgI_4$$

Mercuric sulphide, HgS : When H_2S is passed in a solution of mercuric salts, HgS is precipitated out. The precipitate is first white, then yellow, then red and finally black. It is insoluble even in conc HCl. When the black HgS is heated, red HgS is formed and this is used as a pigment under the name of *vermilion.*

HgS also occurs in nature as cinnabar. HgS is dissolved by aqua regia, $KClO_3$ and alkaline solution of Na_2S :

$$HgS + Cl_2 = HgCl_2 + S$$

$$HgS + Na_2S = Na_2HgS_2$$

When heated, HgS is decomposed to mercury and sulphur or SO_2

Mercuric sulphate, $HgSO_4$: $HgSO_4$ is obtained by heating Hg with conc H_2SO_4 :

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2$$

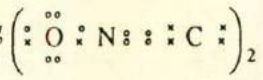
$HgSO_4$ is a white powder and on heating it is decomposed to Hg_2SO_4.

Mercuric nitrate, $Hg(NO_3)_2$: This is obtained by heating Hg with excess of conc HNO_3. It is a deliquescent substance and hydrolysed in water :

$$Hg + 4HNO_3 = Hg(NO_3)_2 + 2NO_2 + 2H_2O$$

$$3Hg(NO_3)_2 + 2H_2O = Hg_3O_2(NO_3)_2 + 4HNO_3$$

Mercuric fulminate, $Hg(ONC)_2$: It is formed by the action of HNO_3 on Hg in presence of alcohol. It is a highly explosive compound and is used as detonators. *Mercury fulminate* may be written as,



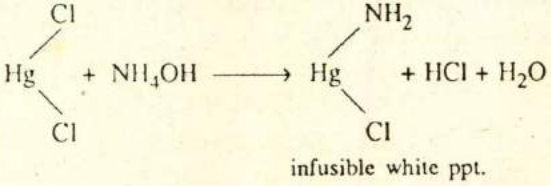
Mercuric Thiocyanate, $Hg(SCN)_2$: It is obtained by mixing mercuric chloride solution with NH_4CNS. It is a white precipitate and when dried and ignited, it evolves a voluminous serpent-like ash known as *Pharaoh's Serpent.*

$$HgCl_2 + 2NH_4SCN = Hg(SCN)_2 + 2NH_4Cl$$

$Hg(SCN)_2$ is very slightly dissociated and mercuric ion in solution may be titrated with a solution of KSCN using ferric salt as an indicator.

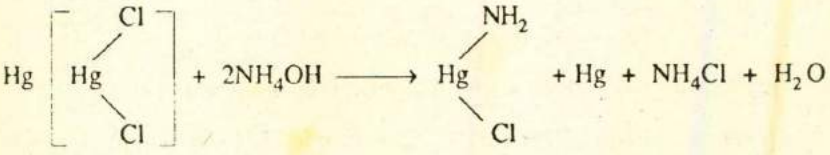
Ammonobasic Compounds of Mercury

When NH_4OH is added to a solution of $HgCl_2$, a white precipitate is obtained, which is not $Hg(OH)_2$ or HgO, but contains N_2 and Cl_2 :

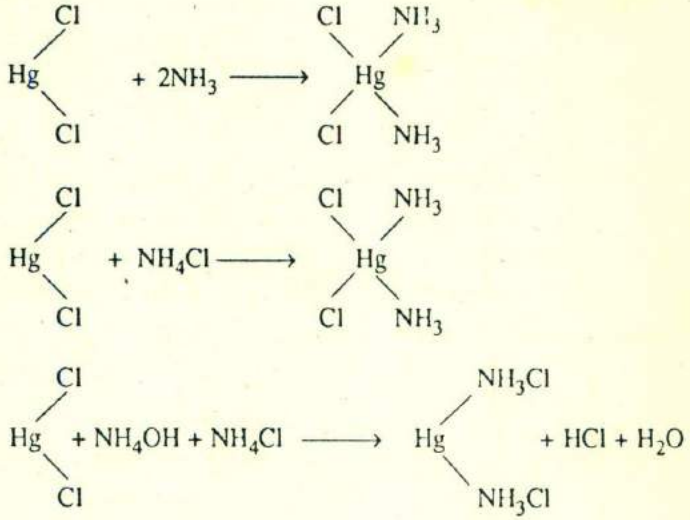


infusible white ppt.

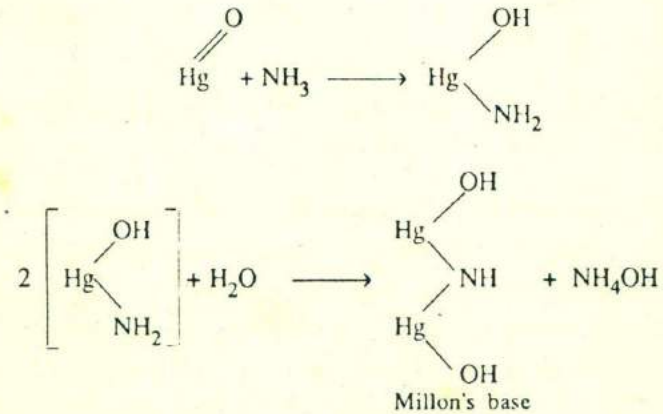
Hg_2Cl_2 gives grey precipitate due to the liberation of Hg along with $Hg(NH_2)Cl$:



The above two reactions are used to distinguish between Hg^{+2} and Hg_2^{+2}. When NH_3 gas is passed over $HgCl_2$, the product is a fusible white precipitate, also obtained in conc NH_4OH and NH_4Cl :

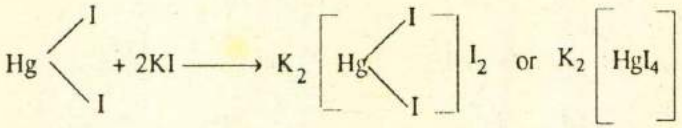


When precipitated HgO is suspended in NH_4OH solution, a pale yellow powder is formed which is called "Millon's base" $2HgO.NH_3$. This is obtained by both ammonolysis and hydrolysis processes :

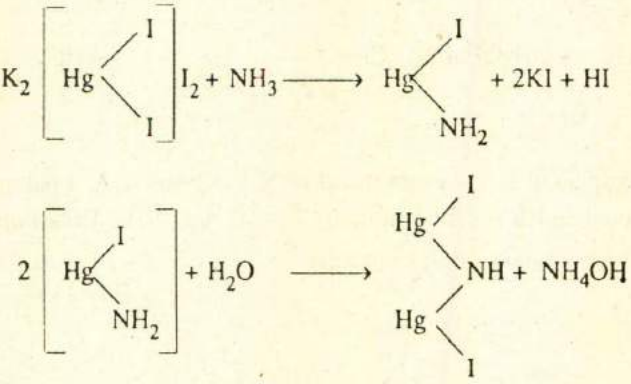


The hydrated form of Millon's base is $Hg_2(OH)_2NH_2OH$.

Nessler's Reagent : When KI is added to a solution of $HgCl_2$, a red precipitate of HgI_2 is first formed which dissolves on adding excess KI forming a colourless solution containing Hg^{+2} ion in the complex form K_2HgI_4.



KOH solution is added to this colourless complex solution of $K_2[HgI_4]$ which is the Nessler's Reagent. This reagent provides a sensitive test for NH_3. When NH_3 gas is passed through the solution or even when an ammonium salt is added to the reagent the liberated NH_3 gives brown precipitate or colouration which is the iodide of Millon's base :



The hydrated form is $Hg_2I_2\,NH_2OH$. The reactions for Nessler's reagent is $2K_2HgI_4 + NH_3 + KOH \longrightarrow NH_2Hg_2I_3 + 5KI + H_2O$.

Complex compounds of Zn, Cd and Hg : Like the coinage metals (IB), the metals of zinc group (IIB) also form a large number of complex compounds. Some complexes have already been mentioned before. The most common complexes are formed by the halides, cyanide and ammonia groups. Most of the complexes possess the tetrahedral structures involving sp^3 bonds as in $Zn(NH_3)_4Cl_2$, $K_2Zn(CN)_4$, K_2HgI_4 etc. Zn and Cd also form 6 coordinated complexes as in $Cd(NH_3)_6Cl_2$ which are considered as outer orbital complexes.

Amalgams : Amalgams are solutions of other metals in mercury. In some cases, such as with Na and K, distinct chemical compounds (Hg_2Na and Hg_2K) are formed with Hg. Iron has the least solubility in mercury, other metals

such as lead, zinc, silver etc. are highly soluble giving amalgams of invariant composition.

QUESTION AND PROBLEMS

1. Write a short note on Nessler's Reagent.
2. Give an account of occurrence, extraction and purification of mercury. Describe the reactions which occur when an aqueous solution of mercuric chloride is treated with an excess of (a) an aqueous solution of potassium iodide, (b) an aqueous solution of stannous chloride, (c) an aqueous solution of sodium hydroxide and (d) copper.
3. Write a brief note on the action of ammonia on salts of mercury and silver.
4. Write short notes on the following :-
   (a) Calomel, (b) Lithopone, (c) Corrosive sublimate and (d) Zinc white.
5. Discuss the comparative chemistry of group IIA and group IIB elements with particular reference to the properties based on electronic configurations.
6. Discuss the principles involved in the extraction of zinc from zinc blende.
7. How can you extract pure zinc from zinc sulphide by the electrolytic process?
8. How will you separate and identify Cd and Cu in a mixture of their solution?
9. Write a note on the ammonolytic compounds of mercury.
10. What are the advantages of galvanizing iron sheets and pipes? Describe briefly the process of galvanizing iron materials by various techniques.
11. Write a short note on the Alkaline Earth metals and their compounds.
12. Show with examples that aluminium and zinc are amphoteric in nature.
13. Give brief description of the preparation and uses of :—
    (a) Calomel, (b) Lithopone, (c) Nessler's Reagent.

CHAPTER 18

BORON AND ALUMINIUM

(Elements of Group III)

The elements of group III are divided into two sub-groups. These are :

Group IIIA	*Group IIIB*
B — Boron	
Al — Aluminium	
Ga — Gallium	Sc — Scandium
In — Indium	Y — Yttrium
Tl — Thalium	La — Lanthanum*

Boron and aluminium are the representative elements of group III of the Priodic Table. Scandium, yttrium, lanthanum and all the rare earth elements may be placed in the sub-group IIIB. Gallium, indium, thalium together with the representative elements boron and aluminium are being placed in the sub-group IIIA. The placements of the elements into A and B sub-groups in this group III and onward is a matter of convenience and sometimes the order is reversed. But boron and aluminium have more common characteristics with Ga, In and Tl and hence all these five may be considered to be the elements of group IIIA. The elements of the subs-group IIIA have 3 electrons s^2p^1 in the outermost energy levels beyond the core of inert gas configurations, whereas those of the sub-group IIIB have three electrons involving **d** and **f** electrons and in most cases the three electrons are beyond a set of 18 electron types. Again, the rare earth

* La and all the other rare earth elements from Ce(58) to Lu (71) may be considered to have similar chemistry and are classified under Rare Earth elements or Lanthanides.

elements together with Sc and Y constitute a group which is rather unique and the chemistry of these elements are discussed separately.

In the elements of group IIIA we encounter the situation where the non-metallic character tends to show itself as in the case of the starting element boron, although the metallic character increases as we go down the group with increasing atomic number.

The Electronic Structure

The electronic configurations of the group IIIA elements are given in Table 18.1.

Table 18.1. Electronic configurations of group IIIA elements.

At. No.	*Elements*	*Electronic configuration*	*Valence electrons*
5	B	He crore, $2s^2\ 2p^1$	$2s^2\ 2p^1$
13	Al	Ne core, $3s^2\ 3p^1$	$3s^2\ 3p^1$
31	Ga	Ar core, $3d^{10}4s^2\ 4p^1$	$4s^2\ 4p^1$
49	In	Kr core, $4d^{10}\ 5s^2\ 5p^1$	$5s^2\ 5p^1$
81	Tl	Xe core, $4f^{14}\ 5d^{10}\ 6s^2\ 6p^1$	$6s^2\ 6p^1$

Thus, from the Table 18.1 we see that the elements of this group have three electrons in the outer orbitals : two are s electrons and one is p electron. The electronic configurations of B and Al may be separately shown as,

B(5)—$1s^2 2s^2 2p^1$

Al(13)—$1s^2 2s^2 2p^6 3s^2 3p^1$

The third electron in p is loosely bond not only because it is unpaired but also because it is at higher energy level than s electrons.

Physical properties : Some of the physical properties of group IIIA elements are given in Table 18.2.

It is the unpaired **p** electron in the outermost orbital which is easily lost and hence the ionization potentials for the elements in this group are slightly less than those for the corresponding elements of group II containing paired electrons in their outer orbitals.

The first element, boron, in this group is distinctly a non-metal and its properties show diagonal relationship with silicon in the next group IV. Boron does not conduct electricity. But aluminium is a true metal with good electrical conductivity and other metallic properties. Some of the points of the comparative chemistry of boron and aluminium are enumerated hereafter.

Table 18.2. Physical properties of group IIIA elements.

Properties	*B*	*Al*	*Ga*	*In*	*Tl*
At. No.	5	13	31	49	81
At. wt.	10.82	26.97	70.10	114.80	204.60
Atomic radius (Å)	0.88	1.43	1.22	1.62	1.71
Ionic radius M^{+3} (Å)	0.20	0.50	0.62	0.81	0.95
Ionization potential M^{+}(ev)	8.03	6.00	6.00	5.80	6.10
Outer electron configuration	$2s^2 2p^1$	$3s^2 3p^1$	$4s^2 4p^1$	$5s^2\ 5p^1$	$6s^2\ 6p^1$
Density (g/cm^3)	2.30	2.70	5.90	7.40	11.80
Melting point (°C)	2300	658	29	155	303
Boiling Point (°C)	2550	1800	1600	1450	1650
Oxidation potential (v)	—	Al/Al^{+3} +1.67	Ga/Ga^{+2} +0.53	In/In^{+2} +0.34	Tl/Tl^{+} +0.34
Electronegativity	2.00	1.50	1.80	1.50	1.44
Oxidation states	+3	+3	+1,+2, +3	+1,+2,+3	+1,+3

Comparative Chemistry of Boron And Aluminium

1. The electronic configurations of boron and aluminium,

B—$1s^2\ 2s^2\ 2p^1$

Al— $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

indicate that in spite of the three electrons in the outermost energy level of the two elements (s^2p^1), there are marked differences in some of the properties. The differences are due to the sizes of atoms and ions of the two elements. There is no real B^{+3} ion because the 3 electrons are held firmly. But Al^{+3} ion having ionic radius 0.5 Å forms many ionic compounds.

2. Some of the physical properties mentioned in Table 18.2 show that boron has a very high melting point (2300°C) and it is a non-metal or semi-metal having properties related to that of silicon. The non-metallic property is due to the small size and high charge of boron. Aluminium has comparatively low melting point (658°C) and is distinctly metallic because Al has a larger size than B, although the charge is the same. High ionization potential of B also gives it non-metallic character.

3. Aluminium is the third most abundant element in the earth's crust whereas boron is almost scarce probably due to the fact that boron nuclei had been transformed into other nuclei by cosmic rays. Boron shows allotropy which is not exhibited by aluminium.

4. Oxidation state of +3 is common both for boron and aluminium but boron has greater tendency to form covalent compounds particularly with hydrogen showing anomalous bonding. KBF_4 has a tetrahedral structure. Al shows coordination number of 4 as in Al_2Cl_6 and in $Al(NH_3)_4Cl_3$ having tetrahedral structure. $Na_3[AlF_6]$ has octahedral arrangement. The octahedral configuration of Al is due to the availability of the vacant 3d orbitals.

5. Boron forms more stable acidic oxide and stable borates are the principal salts of boron. Boric acid and borates occur in nature. Aluminium oxide is amphoteric and aluminates are unstable. The small size of B^{+3} ion pulls electrons to itself from H_2O and ruptures the OH bond giving H^+ ion. Hence $B(OH)_3$ and B_2O_3 are acidic. The large Al^{+3} does not behave in this manner.

6. Halides, sulphates and nitrates of aluminium are common stable compounds of aluminium. Such compounds of boron are also formed but are less stable. Al forms both hydroxide and halide complexes. Aluminium sulphate gives a series of double sulphates known as alums. No such compounds are formed with B.

7. Both aluminium and boron form nitrides, AlN and BN. Boron forms oxide B_2O_3, Al gives Al_2O_3. Hydroxides are $B(OH)_3$ and $Al(OH)_3$.

8. Boron forms B_2H_6, B_4H_{10} and other hydrides. Al does not form similar hydrides.

9. Al is less electronegative than B which has greater tendency to form covalent compounds than Al.

10. Aluminium is an extremely useful structural material whereas boron has only scientific applications.

In accordance with the diagonal relationships in the Periodic Table, boron has similarities in properties with Si and to some extent with carbon. The similarity arises mainly due to the atomic and ionic sizes which are close to each other in B, Si and C.

Comparison of Boron and Silicon

Boron and silicon are members of Group III and Group IV respectively but resemble in chemical properties closely. Boron is regarded as a "bridge elements" because it forms a bridge between Group III and Group IV as in the case of Li and Be which are also bridge elements and show diagonal relationship. The similarity of chemical properties arises due to the fact that the ratio of nuclear charge to atomic radius, Z/r, is nearly the same indicating that the outermost electrons are attracted to the nucleus with about equal force. Electronic structures of B and Si are :

$$B—1s^2\ 2s^2\ 2p^1$$

$$Si—1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$$

Similarities :

(1) B and Si belong to the class of semiconductor. They show increased electrical conductivity at high temperature. This property is unlike metallic characteristic.

(2) B and Si have a number of allotropic forms and are non-metals with little metallic characteristic. Neither occurs free in nature. They are hard and have high melting points indicating strong bonding between the individual atoms. B and Si do not form cations.

(3) Boron and silicon resist the actions of acids and alkalis. On fusion with alkalis both form silicates and borates evolving H_2.

(4) Boron and silicon form large number of hydrides similar to hydrocarbons.

Thus, we have, B_2H_6, Si_2H_6, and C_2H_6 although B_2H_6 has different structure.

(5) BCl_3 and $SiCl_4$ are covalent liquids at ordinary temperature. They are easily hydrolysed by water :

$$BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3HCl$$

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

(6). B and Si form BF_3 and SiF_4 respectively which are colourless gases, covalent and are also easily hydrolysed forming acids.

(7). B_2O_3 and SiO_2 are acidic oxides and form giant molecules by linking of B—O—B, and Si—O—Si bonds in three dimensions respectively.

Dissimilarities :

(1) B and Si have different electronic structures.

(2) B and Si have different atomic radii.

(3) Normal valence of B is 3 whereas that of Si is 4.

(4) Hydrides of B have different structures than those of silicon hydrides which resemble hydrocarbons.

(5) H_3BO_3 is more stable than H_4SiO_4 and occurs in nature.

(6) Borates consists of BO_2^- and BO_3^{-3} ions whereas silicates are made of SiO_4 tetrahedra.

Gradation of Properties in the Group IIIA

Comparison of Al Group : Apart from the variation of properties mentioned in the Table 18.2, the following points regarding the gradation of properties of Group IIIA elements may be indicated :—

(1) Boron is a non-metal with melting point about 2300°C. Crystal structure of B and Al are different. Ga is a metal and almost liquid at ordinary temperature having m. p. 29°C.

Indium is a metal, soft and malleable, m. p. 150°C.

Tl is a metal, soft and malleable and marks paper like lead. The marking vanishes in moist air due to formation of TlOH and Tl_2CO_3. The mobile nature

of the electrons in the outer orbitals increases with the increase in the atomic number.

(2) B has acidic properties and the hydroxide is acidic. Al is amphoteric, $Al(OH)_3$ is insoluble but soluble in acids and alkalis. Ga is more acidic than Al. $Ga(OH)_3$ is soluble in ammonia. In and Tl hydroxides are more basic.

(3) B is extracted from B_2O_3 by reaction with reactive metals. Al is extracted from Al_2O_3 by electrolytic process. Ga_2O_3, In_2O_3 and Tl_2O_3 are easily reduced by hydrogen.

(4) B forms covalent compounds. Al is covalent but also ionic.

In and Tl form compounds having different oxidation states, such as,

$InCl$, $InCl_2$, $InCl_3$

$TlCl$, $TlCl_3$

5. Flame spectra—

Element	*Colour of flame*
B	In conc H_2SO_4 and alcohol, it gives green-edged flame due to the burning of ethyl borate
Al	No colour
Ga	Violet
In	Dark blue
Tl	Green

Extraction of Boron and Aluminium

Extraction of Boron

Sources : Borax — $Na_2B_4O_7.10H_2O$

Boracite — $Mg_3B_8O_{11}.MgCl_2$

Colemanite — $Ca_2B_6O_{11}.5H_2O$

Borocalcite — $CaB_4O_7.4H_2O$

It is also found as boric acid, H_3BO_3, in the hot spring in volcanic regions.

Elementary boron can be extracted by a number of methods starting from minerals and boron compounds.

Extraction of boron from minerals : The minerals are processed in order to convert them to B_2O_3 first. Borax or tincal is treated with hot conc

HCl, whereby sparingly soluble H_3BO_3 is deposited. This on heating gives B_2O_3 which is reduced to elementary B by reduction with Mg.

$$\text{Borax } (Na_2B_4O_7) + HCl \longrightarrow H_3BO_3 + NaCl$$

$$\downarrow \text{heat}$$

$$MgO + B \xleftarrow[\text{heat}]{Mg} B_2O_3 + H_2O$$

Colemanite and other minerals are treated differently as shown below either by Na_2CO_3 or by SO_2 :

(i) Ground colemanite $(Ca_2B_6O_{11}) + Na_2CO_3 \xrightarrow{\text{heat}}$ product

(soln)

$$\downarrow \text{filtered}$$

$$\downarrow \qquad\qquad \downarrow$$

$$H_3BO_3 \xleftarrow{HCl} Na_2B_4O_7 \text{ solution} \xleftarrow{CO_2 \text{ passed}} NaBO_2 + Na_2B_4O_7 \text{ solution} \qquad CaCO_3 \text{ residue}$$

$$\downarrow \text{heat}$$

$$H_2O + B_2O_3 \xrightarrow[\text{heat}]{Mg} B + MgO$$

(ii) Ground colemanite, $Ca_2B_6O_{11}$, is suspended in water and on passing SO_2 through the suspension $CaSO_3$ is precipitated out and H_3BO_3 is isolated from the hot solution on cooling. Elementary boron is obtained by the reduction of B_2O_3 with Mg or with Na :

$$B_2O_3 + 3Mg = 2B + 3MgO$$

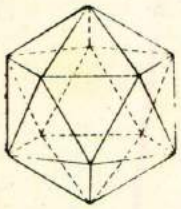
$$B_2O_3 + 6Na = 2B + 3Na_2O$$

MgO remains in the solid product and is removed by dissolving in HCl. Na_2O is washed out by water. Boron prepared by reduction with Mg is impure in the form of a brown amorphous powder.

Pure boron is obtained by passing a mixture of BCl_3 and H_2 through an electric arc or a hot tube.

$$2BCl_3 + 3H_2 = 2B + 6HCl$$

The mixture of BCl_3 and H_2 when passed through a tube containing an electrically heated tungsten (W) filament, pure crystalline boron is formed and deposited in layers on the filament. Boron is metalloid and a semiconductor. It occurs in three allotropic forms. The crystal lattice may consist of icosahedron units (20-sided structure).



An Icosahedron

Extraction of Aluminium

Aluminium is the most abundant metal and the third most abundant element in the earth's crust. It does not occur free in nature and, although most abundant, it was not extracted from its minerals until the end of the 19th century because of the difficulties involved in its extraction.

Sources : Bauxite — $Al_2O_3.2H_2O$
Diaspore — $Al_2O_3.H_2O$
Corundum — Al_2O_3
Cryolite — Na_3AlF_6

[N.B. Very large and widely distributed quantities of Al occur in aluminosilicates such as clays (kaolin), feldspar, mica etc]

Hall and Baeyer's method :

Powder bauxite $\xrightarrow[\text{or } (Na_2CO_3)]{\text{fused with NaOH}}$ fused mass $\xrightarrow{\text{Water extracted}}$ Residue (Ca silicate, $Fe(OH)_3$) + Solution

Solution $\xrightarrow[\text{filtered}]{CO_2 \text{ passed}}$ $Al(OH)_3$ precipitate $\xrightarrow{1200°C,\ \text{heat}}$ Al_2O_3 alumina

The reactions involved are :

$$Al_2O_3.2H_2O + Na_2CO_3 = 2NaAlO_2 + 2H_2O + CO_2$$
$$2NaAlO_2 + 3H_2O + CO_2 = 2Al(OH)_3 + Na_2CO_3$$
$$Al_2O_3.2H_2O + 2NaOH = 2NaAlO_2 + 3H_2O$$
$$2NaAlO_2 + 2H_2O \text{ (dilution)} = Al(OH)_3 + NaOH$$

Serpek's process : This process is suitable for bauxite containing larger amount of silica. The ore is heated with carbon while a stream of nitrogen is passed over the heated mixture forming AlN :

$$Al_2O_3.2H_2O + 3C + N_2 = 2AlN + 3CO + 2H_2O$$

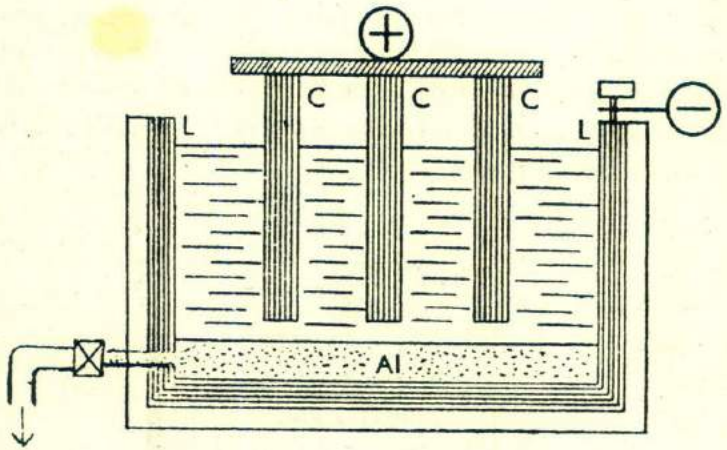
AlN on hydrolysis gives $Al(OH)_3$:

$$2AlN + 6H_2O = 2Al(OH)_3 + 2NH_3$$

$Al(OH)_3$ on calcination produces alumina :

$$2Al(OH)_3 = Al_2O_3 + 3H_2O$$

Electrometallurgy of aluminium (Hall-Herault Process) : The purified bauxite in the form of alumina obtained by the above mentioned processes is used as the starting material for electrometallurgy of Al. Alumina is dissolved in fused cryolite, Na_3AlF_6, and the molten solution is electrolysed in a steel tank lined with carbon in the inside. The lining is made the cathode and the anode is also made of carbon rods which dip in the molten mass as shown in Fig. 18—1.



C—Carbon rods as anodes, L—Carbon lining as cathode, Al—Aluminium in the molten state

Fig. 18—1. Electrolytic cell for the manufacture of Al from Al_2O_3.

The voltage of the cell is adjusted to ensure deposition of aluminium at the bottom but not of sodium which remains in the solution. Although Al_2O_3 is the raw material but in the molten condition in the cryolite, Na_3AlF_6, the formation of some AlF_3 may take place. This on electrolysis gives Al at the cathode :

$$Al^{+3} + 3e^- \longrightarrow Al$$

and at the anode : $6F^- + 6e \longrightarrow 3F_2$

The liberated F_2 immediately reacts with Al_2O_3 forming AlF_3 and oxygen which is evolved at the anode. The overall reaction, therefore, is,

$$2Al_2O_3 = 4Al + 3O_2$$

Na_2AlF_6 acts as catalyst and lowers the melting point of Al_2O_3 mixture to 900°C. The molten Al is drawn off from the tap-hole and more Al_2O_3 is added to the fused electrolyte. The liberated O_2 attacks the carbon anode forming some CO and CO_2. In a modified method, artificial mixture of fluorides are used instead of cryolite. The mixture has an approximate composition of $2AlF_3.6NaF.3CaF_2$.

Al produced by the above methods is 99% pure and contains Cu, Fe, Si, Al_2O_3 etc. as impurities.

Electro-refining of aluminium : 99.9% pure Al is produced by the Hoopes Electrolytic Process. The fused bath consists of three layers. The bottom layer is a fused alloy of Cu-Al, the top layer is pure molten Al and the middle layer consists of the electrolyte of a fused mixture of BaF_2, AlF_3 and NaF saturated with Al_2O_3. The layers are maintained by the difference in their densities during electrolysis. The bottom layer is the anode and the top layer is the cathode as shown in Fig. 18—2.

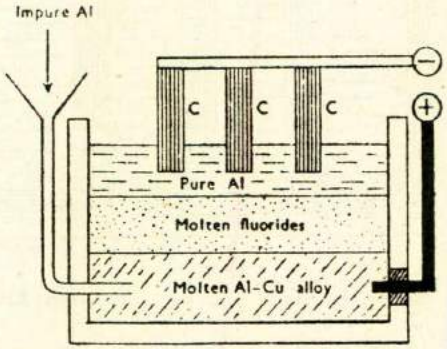


Fig. 18—2. Electro-refining of aluminium.

On electrolysis Al from Cu-Al alloy goes into solution in the middle layer as Al^{+3}, leaving the impurities behind at the anode. The Al^{+3} is now reduced at the cathode and the upper layer of Al grows which is drawn off and impure metal is added to the bottom layer. Al obtained is pure.

Uses of Boron and Aluminium

Uses of Boron : Boron as such has not many uses except in making special compounds of boron as boron carbides and borides. These are hard materials and used as abrasives. Boron rods are also used in nuclear reactors for controlling the neutron flux because boron acts as a good neutron absorber. Boron is used in the purification of pure copper for casting.

Other important useful compounds of boron are made from B_2O_3, borax, boric acid and even directly from the minerals.

Uses of Aluminium

(1) Al is used in making cooking utensils because of its light weight, resistance to corrosion and chiefly because it is a good conductor of heat.

(2) Aeroplane bodies and other structural materials are made of Al.

(3) Aluminium is used in paints and pigments.

(4) For reflecting heat and light in reflecting mirrors.

(5) Making special types of alloys such as.

(a) Duralumin : Al—92.5%, Mg—1.5%, Cu—4%, Ni—2% (or Cu—2% and Ni—4%). This alloy is light but is strong as steel and specially used in aircraft. In order to further protect it from corrosive action of air, the alloy is given a coating of thin layer of pure Al, the product is known as Alcald.

(b) Al—Bronze : Cu—90%, Al—10%. This is golden in colour, has great tensile strength and is used in jewellery.

(c) Alnico : Fe—50%, Al—20%, Ni—2%, Co—10%. This is a magnetic alloy and can lift huge pieces of iron. This is produced by pressing the metals in powder form just below the melting point and is an example of a new metallurgical technique known as ***Powder Metallurgy***.

(d) Magnalium : Al—95 to 70%, Mg—5 to 30%. It is used for producing cheap goods.

Aluminothermic process : This is also known as *Thermite process* or *Goldschmidt Thermic process*. Aluminium powder is used for this reaction for the purpose of reducing metallic oxides to metals particularly those of Cr, Mn, Mo, W etc. Fe_2O_3 can also be reduced to Fe by this process. The thermite consists of a mixture of metallic oxide with Al powder together with a little BaO_2 in a crucible lined with magnesia having a hole at the bottom. The thermite mixture is ignited with the help of a fuse of magnesium ribbon as shown in Fig. 18—3.

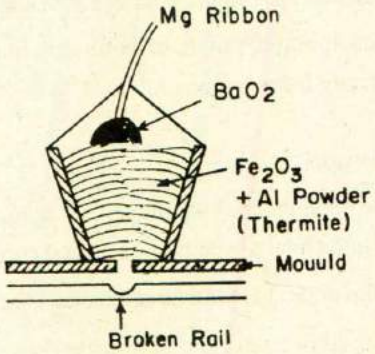


Fig. 18—3. Sketch of aluminothermic process.

Considerable temperature is generated upto 3000°C due to exothermic reaction so that Fe and Al_2O_3 become liquid :

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$$

The molten metal by suitable method may be used for welding broken pieces of steel, such as, rail and other materials.

Because of the high temperature in the thermite reaction which is not readily quenched by water, the thermite bombs have been used for incendiary purposes. The high temperature results from the high heat of formation of Al_2O_3 (solid) :

$$4Al + 3O_2 \longrightarrow 2Al_2O_3 \quad \Delta H = -399 \text{ Kcal/mole } Al_2O_3$$

During the reaction with Fe_2O_3, the heat evolved is sufficient to produce Fe and Al_2O_3 in the molten state.

Compounds of Boron and Aluminium

Some important compounds of boron and aluminium are described here briefly.

Compounds of Boron

Boron hydrides : Boron forms a series of volatile hydrides similar to the hydrides of C and Si having compositions from B_2H_6 to $B_{10}H_{14}$. The simplest boron hydride, BH_3, does not exist and is dimerized to B_2H_6 (diborane). The boron hydrides are generally known as boranes. There are two series of boranes :

B_nH_{n+4} where n=2, 5, 6 and 10

B_nH_{n+6} where n=4, 5 and 9

These are prepared by hydrolysis of Mg_3B_2 :

$$B_2O_3 + 6Mg \xrightarrow{\text{heat}} Mg_3B_2 + 3MgO$$

$$\downarrow \text{dil. HCl}$$

$$B_2H_6 + \text{other boranes}$$

$$\downarrow \text{condensed in liquid air}$$

$$\text{Boranes separated} \xleftarrow[\text{distillation}]{\text{fractional}} \text{liquid boranes}$$

Diborane, B_2H_6, has also been prepared by passing BCl_3 vapour and H_2 through a tube and subjecting the mixture to an electric discharge :

$$2BCl_3 + 5H_2 = B_2H_5Cl + 5HCl$$

$$6B_2H_5Cl = 5B_2H_6 + 2BCl_3$$

Diborane is more easily formed by the action of $LiAlH_4$ or LiH on BCl_3 in ether solution :

$$4BF_3 + 3LiAlH_4 = 2B_2H_6 + 3LiF + 3AlF_3$$

B_2H_6 decomposes slowly forming higher boranes. When heated to 300°C, B_2H_6 is decomposed to B + H_2. It is readily hydrolysed by water forming $H_3BO_3 + H_2$:

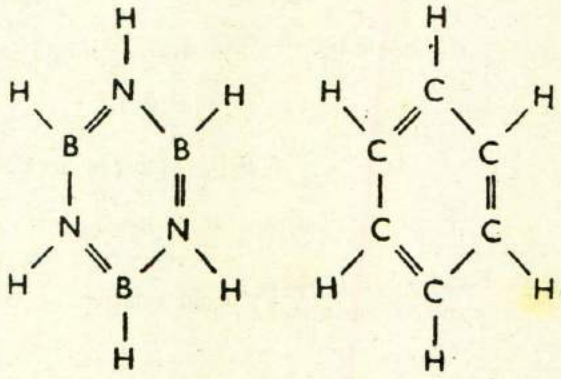
$$B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$$

Many of the reactions of B_2H_6 give indication of the reaction of the "half molecule" BH_3. Thus,

$$(CH_3)_3\,N{:}\,BH_3 \text{ and } CH_3CN{:}\,BH_3$$

B_2H_6 and boranes are easily flamable in air. The boranes have been used as rocket fuel and jet fuel since they have high heats of combustion and low mol. wt. The energy obtained per g. of B_2H_6 is very high.

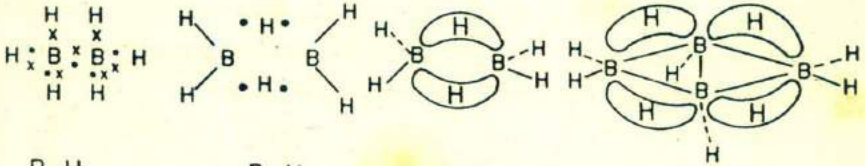
B_2H_6 has an interesting reaction with NH_3 giving first $B_2H_6.2NH_3$ which on heating forms $B_3N_3H_6$ which is an electronic isomer of benzene known as *borazol* or *borazine* as shown below.



Borazine Benzene

Structure of B_2H_6 : Much work has been done on the structure of boranes and this has been a puzzling problem in inorganic chemistry. An electronic structure for B_2H_6 cannot be written since there are only 12 electrons to form 7 covalent bonds between B and H in B_2H_6. B_2H_6 is, therefore, regarded as an "electron deficient" compound. Various structures have been suggested and only two representative structures are given indicated by (I) and (II).

The modern view about the structures of B_2H_6 and other boron hydrides is that the bridge H atom between two B atoms participates in a three-centre bond formed by two electrons (single pair). Boron hydrides have prospective use as rocket fuels.



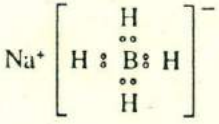
B_2H_6 B_2H_6 B_2H_6 B_4H_{10}

Each bridge H joins two B atoms by three-centre BHB bonds.

Sodium borohydrides, $NaBH_4$: This is obtained by the action of NaH on BF_3 in ether solution :

$$4NaH + BF_3 \xrightarrow{\text{ether}} NaBH_4 + 3NaF$$

Similarly, $LiBH_4$ is also obtained. In this compounds 4H are covalently bonded to B forming BH_4^- ion (tetracovalent B) having tetrahedral sp^3 structure.



$LiBH_4$ and other borohydrides are used as versatile reducing agents in organic chemistry and also in inorganic synthesis for the preparation of unstable hydrides.

Boron nitride, BN : Boron forms quite a large number of compounds with B—N bonds. BN is formed by heating B in N_2 at 1000°C :

$$2B + N_2 = 2BN$$

It is also made by reaction of BCl_3 and NH_3 :

$$BCl_3 + NH_3 = BN + 3HCl$$

Also by thermal decomposition of $F_3B : NH_3$:

$$F_3B : NH_3 \xrightarrow{\text{heat}} BN + 3HF$$

BN and graphite (C) have similar giant layer structure. This is because the atomic radius of C is almost equal to half the sum of the atomic radii of B and N. Carbon lies in between B and N in the Periodic Table. In BN the layers consist of alternate B and N atoms. It is very stable and has high melting point (3000°C). It reacts with water slowly to give H_3BO_3 and NH_3 :

$$BN + 3H_2O = H_3BO_3 + NH_3$$

The presence of H_3BO_3 in hot spring of volcanic origin is attributed due to the hydrolysis of BN of volcanic origin. Boron nitride is very hard and the crystalline variety has the diamond-like hardness and is used as abrasive.

Boron halides, BX_3: Boron fluoride is made by the action of B_2O_3, H_2SO_4 and a fluoride, such as CaF_2 :

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 = 3CaSO_4 + 3H_2O + 2BF_3$$

BCl_3 is made by the action of BF_3 on $AlCl_3$ by heat :

$$BF_3 + AlCl_3 = AlF_3 + BCl_3$$

This is also made by heating B_2O_3 mixed with C and passing a stream of Cl_2 :

$$B_2O_3 + 2C + 3Cl_2 = 2BCl_3 + 3CO$$

With PCl_5 :

$$B_2O_3 + 3PCl_5 = 3POCl_3 + 2BCl_3$$

BBr_3 is made in a similar manner from B_2O_3, C and Br_2 :

$$B_2O_3 + 3C + 3Br_2 = 2BBr_3 + 3CO$$

BI_3 is made by heating B in HI :

$$2B + 6HI = 2BI_3 + 3H_2$$

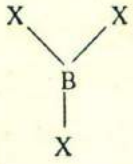
The boron halides can also be made by the direct union of B and the halogens but the method is inconvenient.

BF_3 is a gas, BCl_3 and BBr_3 are liquids and BI_3 is solid at ordinary temperature. They are covalent compounds and Lewis acids.

These are hydrolysed by H_2O to H_3BO_3 :

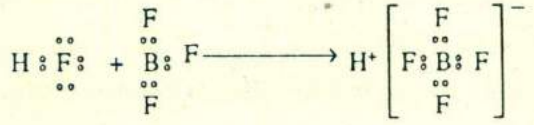
$$BX_3 + 3H_2O = H_3BO_3 + 3HX$$

The three halogens in BX_3 are at the corners of an equilateral triangle giving structures :



This is due to the use of sp^2 hybrid bond orbitals by boron atom forming three equivalent bonds with 3 halogen atoms as illustrated in Fig. 2—10. page

BF_3 being a Lewis acid combines with HF to give HBF_4 and also salts like KBF_4 :



BF_3 is used as a versatile catalyst in organic chemistry.

Boric acid, H_3BO_3 : Ortho-boric acid, H_3BO_3, occurs in nature in the jets of steam known as soffioni in volcanic region since H_3BO_3 is volatile with steam.

(1) It is isolated by evaporating the water and crystallising solid H_3BO_3.

(2) H_3BO_3 can be obtained from colemanite, $Ca_2B_6O_{11}.5H_2O$, by passing SO_2 through a suspension of the mineral in water :

$$Ca_2B_6O_{11} + 4H_2O + 4SO_2 = 2Ca(HSO_3)_2 + H_4B_6O_{11}$$

$$H_4B_6O_{11} + 7H_2O = 6H_3BO_3$$

The overall reaction :

$$Ca_2B_6O_{11} + 11H_2O + 4SO_2 = 2Ca(HSO_3)_2 + 6H_3BO_3$$

(3) Borax, $Na_2B_4O_7$, when treated with conc H_2SO_4 gives boric acid crystals :

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O = Na_2SO_4 + 4H_3BO_3$$

Boric acid, also known as *borasic acid*, is a colourless crystalline substance and soapy to touch because of layer structure. It is sparingly soluble in cold water but dissolves in hot water forming a weak acid solution. It ionizes as,

$$H_3BO_3 \rightleftharpoons H^+ + H_2BO_3^-$$

H_3BO_3 loses H_2O at 100°C forming meta-boric acid, HBO_2, and at 140°C to tetraboric acid. On strong heating, it gives B_2O_3 :

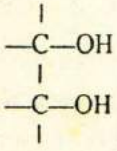
$$H_3BO_3 = HBO_2 + H_2O$$

$$4HBO_2 = H_2B_4O_7 + H_2O$$

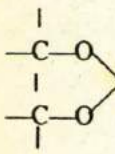
$$H_2B_4O_7 = 2B_2O_3 + H_2O$$

B_2O_3 forms a glassy mass and is mainly used to make borosilicate glasses which resist chemical action and heat.

H_3BO_3 is converted to a strong acid by adding to its solution some organic substances having the group :

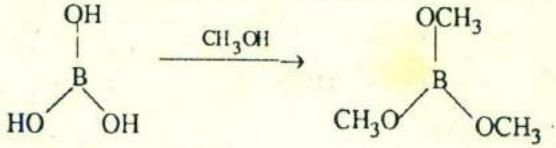


These are glycerine, glucose, mannitol etc. probably forming



B(OH) group which dissociate to give H^+. This is used as a method for the titrimetric determination of boric acid and boron with standard alkali solution in presence of phenolphthalein.

H_3BO_3 also forms methyl and ethyl borates which are volatile compounds and burn with green-edged flame on ignition and this is used to detect borate in qualitative test :



boric acid methyl borate

Boric acid is used as a mild antiseptic. H_3BO_3 is associated in the solid state to form a giant molecule through H-bonding.

Borax, $Na_2B_4O_7.10H_2O$: This is also known as sodium tetraborate or pyroborate. This occurs in nature known as "tincal". It is obtained : (i) from tincal by leaching the mineral with water and crystallising to $Na_2B_4O_7$; (ii) from colemanite by digesting the mineral with conc Na_2CO_3 solution to give $Na_2B_4O_7$ by double decomposition :

$$Ca_2B_6O_{11} + 2Na_2CO_3 = 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$$

$NaBO_2$ is converted to $Na_2B_4O_7$ by CO_2 :

$$4NaBO_2 + CO_2 = Na_2CO_3 + Na_2B_4O_7$$

On crystallisation from aqueous solutions above 58°C, $Na_2B_4O_7.5H_2O$ is obtained, whereas below 58°C, $Na_2B_4O_7.10H_2O$ is obtained. A strong solution of $Na_2B_4O_7$ appears to be acidic whereas a dilute solution is strongly alkaline because NaOH formed is a strong base and H_3BO_3 is a weak acid :

$$Na_2B_4O_7 + 3H_2O = 2NaBO_2 + 2H_3BO_3 \text{ (acidic)}$$

$$Na_2B_4O_7 + 7H_2O = 2NaOH + 4H_3BO_3 \text{ (alkaline)}$$

Uses of Borax : (1) As a laboratory reagent for borax bead tests for some metals. When borax, $Na_2B_4O_7.10H_2O$, is heated on a platinum loop, it first swells due to the escape of H_2O and then melts to form a transparent glassy bead. If a pinch of salts of other metals is fused with it, the metals form metaborates of various colours. Thus, with CoO gives the following reaction :

$$Na_2B_4O_7 + CoO = 2NaBO_2 + Co(BO_2)_2$$

$Co(BO_2)_2$ is coloured blue. Similarly, $Cu(BO_2)_2$ is blue-green, $Cr(BO_2)_3$ is ...en, and $Mn(BO_2)_2$ is amethyst or violet coloured. The colour also changes in

oxidizing and reducing flames and also gives different colours in the cold and hot conditions.

(2) Borax is used as flux for solders.

(3) Food preservation.

(4) Buffer solutions.

(5) Enamels, borosilicate glass, or "pyrex" glass.

(6) Leather industry for soaking and cleaning hides.

Sodium peroxyborate (Sodium perborate),$NaBO_2.H_2O_2.3H_2O$: This is formed from borax solution when treated with NaOH and H_2O_2 giving transparent crystals of $NaBO_2.H_2O_2.3H_2O$. This is used as bleaching agent and as an antiseptic. Na-perborate can be formed by the action of sodium hydroperoxide, $NaHO_2$, on H_3BO_3. It liberates H_2O_2 on hydrolysis and is used as an oxidizing and a bleaching agent.

Compounds of Aluminium

Aluminium oxide (Alumina), Al_2O_3 : In the pure form Al_2O_3 occurs in nature as corundum. It is very hard and is used as abrasive for grinding and polishing. Bauxite is a mineral of Al_2O_3 containing large number of impurities. Emery contains Al_2O_3 together with Fe_2O_3. Ruby contains Al_2O_3 and some Cr_2O_3. Saphire, amethyst etc. are also Al_2O_3 containing impurities. These are precious stones and are used as jewellery. Now-a-days all these are made by artificial processes and are largely used as bearings (jewels) in watches and other instruments. Artificial corundum is known as alundum. Large number of minerals containing Al_2O_3, SiO_2 etc. also occur as precious stones, such as jade, topaz, garnet, aquamarine, tourmaline etc.

Finely divided Al_2O_3 is called *activated alumina* and is used as catalyst, dehydrating agents and in chromatography.

Pure Al_2O_3 is obtained by igniting $Al_2(SO_4)_3$, or $Al(OH)_3$ or alum :

$$Al_2(SO_4)_3 = Al_2O_3 + 3SO_3$$

$$2Al(OH)_3 = Al_2O_3 + 3H_2O$$

Naturally occurring Al_2O_3 is unreactive, but Al_2O_3 prepared in the laboratory is distinctly amphoteric. Al_2O_3 is used in Al metallurgy.

Al_2O_3 is amphoteric :

$$Al_2O_3 + 6H_3O^+ \rightleftharpoons 2Al^{+3} + 9H_2O$$

$$Al_2O_3 + 2(OH)^- + 3H_2O \rightleftharpoons 2Al(OH)_4^-$$

Freshly prepared alumina reacts slowly with water to give AlO.OH (disapore) :

$$Al_2O_3 + H_2O = 2AlO.OH$$

Aluminium hydroxide., $Al(OH)_3$: When alkali is added to a solution of Al-salts, the white gelatinous precipitate formed is $Al(OH)_3$. In excess caustic alkalis the precipitate is soluble forming aluminate :

$$Al^{+3} + 3NaOH = Al(OH)_3 + 3Na^+$$

$$Al(OH)_3 + 3NaOH = Na_3AlO_3 + 3H_2O$$

Solutions of sulphides and carbonates also precipitate $Al(OH)_3$ due to hydrolysis of S^{-2} and CO_3^{-2} ions :

$$S^{-2} + H_2O \rightleftharpoons HS^- + OH^-$$

$$CO_3^{-2} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

The gelatinous precipitate has great tendency to take up colouring matters, such as diazo compounds, alizarine etc. and forms beautiful colours known as "lakes". This is used in dyeing and mordanting of fabrics. Fast colour on cloth is imparted by dipping in a solution of Al-salt, such as Al-acetate. The fibre becomes impregnated with $Al(OH)_3$ due to the hydrolysis of Al-salt. If the solution of Al-salt is mixed with a dye, the precipitate of $Al(OH)_3$ is coloured which is absorbed in the fabrics which hold the colour fast. $Al(OH)_3$ is known as a *Mordant* and the coloured product is called a *Lake*.

Aluminium hydroxide is also used for purification of water.

Aluminium halides, AlX_3 : Aluminium reacts readily with halogens rather vigorously forming AlX_3. The fluoride, AlF_3, is a definite ionic compound and is also obtained when Al is dissolved in HF or when $Al_2(SO_4)_3$ is

heated with NaF. AlF_3 is insoluble in water and not hydrolysed ordinarily but only when heated with steam.

Aluminium chloride, $AlCl_3$, is obtained by various methods :—

(i) Direct reaction between Al-metal and dry chlorine or hydrogen chloride gas in a heated tube gives anhydrous $AlCl_3$ which sublimes and collects in a receiver bottle out of contact with air :

$$2Al + 3Cl_2 = 2AlCl_3$$

(ii) Alumina mixed with carbon heated in dry chlorine gives anhydrous $AlCl_3$:

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO$$

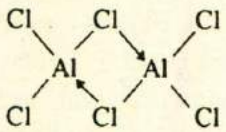
(iii) Alumina heated with sulphur chloride, S_2Cl_2, vapour and chlorine :

$$4Al_2O_3 + 2S_2Cl_2 + 9Cl_2 = 8AlCl_3 + 6SO_2$$

$AlCl_3$ is a white crystalline substance which sublimes at 193°C and is soluble in organic solvents. This is very hygroscopic and a solution in water gives crystal of $Al_2Cl_6.12H_2O$ which cannot be made anhydrous because of hydrolysis :

$$Al_2Cl_6.\ 12H_2O \rightarrow Al_2O_3 + 6HCl + 3H_2O$$

Measurement of vapour density indicates that $AlCl_3$ is a dimer having Al tetrahedrally bonded to four Cl. One Cl of each $AlCl_3$ donates a pair of electrons to be shared by the atom of the other molecule :



Anhydrous $AlCl_3$ is used as a catalyst in many organic reactions and in cracking process for making gasoline. Like BCl_3 it is a strong Lewis acid. In addition to their uses in organic chemistry, $AlCl_3$ and $AlBr_3$ are used to make complex Al-hydrides and alkayls, such as $Al_2(CH_3)_6$.

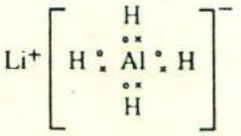
$LiAlH_4$: Al does not react with H_2, but $AlCl_3$ reacts with, say, LiH, in ether to form $LiAlH_4$:

$$AlCl_3 + 4LiH \xrightarrow{\text{ether}} LiAlH_4 + 3LiCl$$

$LiAlH_4$ is decomposed by H_2O :

$$LiAlH_4 + H_2O \rightarrow LiOH + Al(OH)_3 + 4H_2$$

$LiAlH_4$ is an important reducing and hydrogenating reagent. The structure of $LiAlH_4$ contains Li^+ and AlH_4^- ions :



Aluminium Sulphate, $Al_2(SO_4)$: This is prepared from freshly precipitated $Al(OH)_3$ and H_2SO_4. Large quantities of $Al_2(SO_4)_3$ is produced by treating bauxite or clay with H_2SO_4. The aqueous solution on crystallisation gives $Al_2(SO_4)_3$ with 18 or 9 H_2O depending on temperature:

$$Al_2Si_2O_5(OH)_4 + 3H_2SO_4 = Al_2(SO_4)_3 + 5H_2O + 2SiO_2$$

$Al_2(SO_4)_3$ is the cheapest Al-salt soluble in water, and is used for (i) purification of water, (ii) dyeing of fabrics, (iii) in styptic or blood-clotting formulations, (iv) in tanning agents for hides, (v) water proofing and (vi) sizing of papers.

Alums : Alums are made from $Al_2(SO_4)_3$ which are quite numerous. Alums are double or mixed sulphates of Al and some other metal with usually $24H_2O$ in the double salt. The common alum is K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$. K_2SO_4 may be replaced by sulphates of other alkali metals, silver, ammonium and also $Al_2(SO_4)_3$ may be replaced by sulphates of trivalent metal, such as Fe, Cr, Mn etc. Thus chrome alum is K_2SO_4, $Cr_2(SO_4)_3$, $24H_2O$. Ferric alum, K_2SO_4, $Fe_2(SO_4)_3$, $24H_2O$ etc.

Al-alum or potash alum, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$ is produced by the following processes :

(1) Bauxite + H_2SO_4 $\xrightarrow[\text{\& filtered}]{\text{boiled}}$ solution

$\downarrow$ $+K_2SO_4$ evaporated

$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$ crystals

(2) Alunite or Alum stone $\xrightarrow{\text{calcined}}$ dry mass
$K_2SO_4 . Al_2(SO_4)_3 . 4Al(OH)_3$

$\downarrow$ H_2SO_4 filtered

$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O \xleftarrow[\text{evaporated}]{H_2SO_4}$ solution
crystals

Alums are soluble in water and when strongly heated produce porous mass. Alums form very beautiful octahedral crystals.

Alums are mixed crystals and no complex ions are present. The solution gives the test of all the ions present in the crystals indicating complete dissociation. The distribution of 24 molecules of water is as follows :

$2K^+$ ion hydrate— ($4H_2O$ each K^+) $8H_2O$
$2Al^{+3}$ ion hydrate — ($6H_2O$ each Al^{+3}) $12H_2O$
$4SO_4^{-2}$ ion hydrate — (H_2O each SO_4^{-2}) $4H_2O$
} $24H_2O$

Alum is the most important commercial compound of Al and is used in (i) water purification, (ii) dyeing of fabrics, (iii) coagulation of colloidal solutions, (iv) tanning agents for hides, (v) sizing of paper etc.

Aluminium nitride, AlN : On heating, Al combines with N_2 forming AlN :

$$2Al + N_2 = 2AlN$$

It is-also obtained by strong heating of a mixture of bauxite and carbon in a current of N_2 :

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO$$

AlN is a covalent compound of high melting point. It forms a giant molecule having diamond-like structure. The structure is due to the presence of one pair of electrons in nitrogen atoms which are used to form coordinate bonds resulting in a three-dimensional lattice. AlN is isoelectronic with SiC and both

are physically similar. But AlN is rapidly attacked by water or dilute alkali to give ammonia and $Al(OH)_3$:

$$AlN + 3H_2O = Al(OH)_3 + NH_3$$

Aluminium silicates: Many of the most important silicate rocks contain aluminium. Clay and sand are formed by the weathering of rocks. Weathering involves the thawing and freezing of water in the rocks, and the chemical action of water and carbondioxide upon them. The chemical disintegration of feldspar may be represented by the equation :

$$\underset{\text{feldspar}}{2KAlSi_3O_8} + 2H_2O + CO_2 = K_2CO_3 + \underset{\text{clay}}{Al_2Si_2O_5(OH)_4} + \underset{\text{sand}}{4SiO_2}$$

The soluble potassium carbonate formed is largely removed by water, and sand-clay remains as soil. Pure clay shown above is white in colour and is called *kaolin*. Ordinary clay is coloured by compounds of iron and other metals. Kaolin is used for making porcelain china wares, white impure clays are used in the manufacture of earthen wares. The red colour in these earthen-wares is due to the presence of iron silicate. Porous products are obtained by firing, but by means of glazing agents they are made smooth, shining and water-tight. During firing sodium chloride is added in the kiln which makes Na–Al silicate which fills the pores. Better quality china and porcelain wares are glazed by means of feldspar, silica and red oxide during the second firing. The coloured glazes are imparted with the help of suitable metal oxides.

The Elements of Group IIIB

Scandium, Yttrium and the Rare Earths

Scandium(21) and Yttrium(39) are transition metals and have no relationship with the group of elements commonly known as *Rare Earths* so far as the electronic configurations are concerned. But their chemical properties have great similarity with those of the Rare Earths and the atomic numbers relationship places these in the same group IIIB. The Rare Earth elements generally known as *Lanthanides* have themselves been placed together in the

same position of the Periodic Table although starting from *Lanthanum* (57) to *Lutecium* (71), they consist of 15 elements. But generally Lanthanides start from Ce(58)

The Rare Earths (Lanthanides)

These elements from Ce(58) to Lu(71) have physical and chemical properties which are very similar. Their occurrence in nature together and the remarkable similarity in their properties have been attributed due to their similar electron arrangements. The increase in the nuclear charge (atomic number) from Ce (58) to Lu (71) is compensated by placement of the electrons in the 4f and 5d sub-levels rather than the outer orbitals. Their electron arrangements are shown in Table 18.3.

Table 18.3. Electron arrangements of the lanthanides.

Elements	*At. No.*	*Electron configuration*		
La	57	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}$	$4f^0\ 5s^2 5p^6 5d^1$	$6s^2$
Ce	58		$4f^1\ 5s^2 5p^6 5d^1$	$6s^2$
Pr	59		$4f^3\ 5s^2 5p^6 5d^0$	$6s^2$
Nd	60		$4f^4\ 5s^2 5p^6 5d^0$	$6s^2$
Pm	61		$4f^5\ 5s^2 5p^6 5d^0$	$6s^2$
Sm	62		$4f^6\ 5s^2 5p^6 5d^0$	$6s^2$
Eu	63		$4f^7\ 5s^2 5p^6 5d^0$	$6s^2$
Gd	64		$4f^7\ 5s^2 5p^6 5d^1$	$6s^2$
Tb	65		$4f^9\ 5s^2 5p^6 5d^0$	$6s^2$
Dy	66		$4f^{10}\ 5s^2 5p^6 5d^0$	$6s^2$
Ho	67		$4f^{11}\ 5s^2 5p^6 5d^0$	$6s^2$
Er	68		$4f^{12}\ 5s^2 5p^6 5d^0$	$6s^2$
Tm	69		$4f^{13}\ 5s^2 5p^6 5d^0$	$6s^2$
Yb	70		$4f^{14}\ 5s^2 5p^6 5d^0$	$6s^2$
Lu	71		$4f^{14}\ 5s^2 5p^6 5d^1$	$6s^2$

Due to the filling up of **4f** orbitals in the lanthanides a unique feature arises among these group of elements. The electrons in the 4f are nearer the nucleus and hence these are attracted more than the electrons in the outermost energy levels. Thus the atomic size of the elements and so also the ionic size

decrease from lanthanum to lutecium in a systematic manner. This decrease in the atomic or ionic sizes of the rare earth elements is known as *Lanthanide Contraction.*

The rare earth elements are often found together in the minerals. *Monazite sand* is the most important mineral in which the rare earths are present as phosphate together with thorium. There is one exception : element number 61, promethium, which does not occur in nature at all.

Separation of Rare Earths

Due to the Lanthanide contraction the rare earth elements resemble so closely that their separation from one another had been a great problem in chemistry. (1) Fractional crystallisation of their nitrates or double sulphates involving many hundreds of steps led only to partial separation. (2) Recently ion-exchange technique has been used to provide more effective and rapid separation of rare earths by selective absorption of the ions of rare earth on a column of an ion-exchange resin. The absorbed ions are then eluted out by a suitable solvent, such as ammonium acetate or citric acid. It has been observed that the rare earths are eluted out in the reverse order of their atomic number. That is, Lu first and La last. (3) Solvent extraction process has also been developed for the separation of lanthanides.

Properties : The rare earth elements are all silvery white metals of inner transition series with high densities. They form oxides of the general formula M_2O_3 and chlorides MX_3. But Ce shows oxidation states of +4. The normal oxidation state of all the rare earths is +3. Some rare earths show oxidation state +2, e. g., Lu. The basicity of their hydroxides $M(OH)_3$ decreases due to decrease in the ionic size of M^{+3} ions in the group.

CeO_2 mixed with ThO_2 is used in gas mantles. "Misch metal", a mixture of iron and some rare earth metals, is used to make artificial flints for cigarette lighters. Rare earth fluorides are used as the core of the carbon used in the projectors in motion pictures.

QUESTIONS AND PROBLEMS

1. How is borax prepared? Describe the chemistry of the borax bead test.

Discuss the diagonal relationship between boron and silicon.

Write electronic structure for NH_3 and BF_3. These molecules combine to form

the addition compounds NH_3BF_3. What is the electronic structure of this compound? What similarity is there in the following chemical reactions?

$$NH_3 + H^+ \longrightarrow NH_4^+$$
$$NH_3 + BF_3 \longrightarrow NH_3{-}BF_3$$

4. Justify the inclusion of iron and aluminium, widely separated groups of the periodic classifications into the same analytical group. Emphasize the difference between the compounds of these two elements.
5. Discuss the use of borax in analytical chemistry. Give balanced equations for the reaction involved.
6. Write a clear note on alumino-thermit process with reactions involved.
7. What are the sources of aluminium metal? Describe its extraction and important properties.
8. Describe the preparation and properties of anhydrous aluminium chloride.
9. Write a short note on rare earths.
10. Write a short note on Thermit Process.
11. Compare the chemistry of boron and aluminium and their important compounds.
12. Describe the preparation, structure and properties of boron hydrides.
13. Starting with bauxite, how would you prepare—(a) different types of alumina, (b) anhydrous aluminium chloride, and (c) potash alum? Discuss properties and uses of metallic aluminium and its alloys.
14. How bauxite is purified for obtaining pure alumina? Describe the electrolytic process employed for the extraction and refining of aluminium. Discuss the important uses of the metal.
15. Write short note on extraction and refining of aluminium.
16. Compare the chemistry of Boron and Aluminium.
17. Compare the chemistry of Group III elements with particular reference to Boron and Aluminium.
18. Write a note on diborane.
19. Show with examples that aluminium is amphoteric in nature.
20. Give the structure of aluminium chloride.
21. Discuss similarity of properties of boron and silicon.
22. Al is a major metal in our society. Describe the chemistry of its recovery from ores.
23. Al is not recovered from the silicate ores which occur abundantly. Explain why.
24. pH is an important factor in the refining of Al. Why?

25. Why Anhydrous $AlCl_3$ behaves as a Lewis Acid?
26. Differentiate between the Baeyer Process, the Hall-Heralt process and the Hoopes Process of manufacture of Al.
27. Why alum is acidic in aqueous solution?
28. Explain lanthanide contractions.
29. How the rare earth metals are separated from one another?

CHAPTER 19

CARBON AND SILICON

(The Elements of Group IV)

The elements of Group IV are divided into two sub-groups as discussed in connection with the periodic classifications. Carbon and silicon are the two non-metals in Group IV and along with the metals germanium, tin and lead they are placed in Group IVA. The Group IVB are metals—titanium, zirconium and hafnium to which sometimes thorium is included. But Th is now generally placed in the Actinide series of elements. Thus the Group IV elements may be divided into A and B sub-groups as,

Group IV A	*Group IV B*
C — Carbon	
Si — Silicon	Ti — Titanium
Ge — Germanium	Zr — Zirconium
Sn — Tin	Hf — Hafnium
Pb — Lead	

The Group IV elements lie in the middle positions between alkali metals and halogens since each one has 4 valence electrons, i. e., 4 more electrons than the preceding inert gas and 4 fewer electrons than the succeeding inert gas. The carbon group may be regarded as a transition group linking metals and non-metals due to their symmetrical placements in the Periodic Table. But if we remember the relative electronegativity of the carbon group elements (IVA) and knowing that elements having similar power of attracting electrons to themselves lie on the "diagonal lines," the difference in chemical behaviour of the group as a whole can be understood. The diagonal relationships between B and Si have been discussed in the previous chapter.

Electronic Structure

The electronic structures of Group IVA elements are given in Table 19.1

Table 19.1. Electronic structure of Group IVA elements.

At. No.	*Elements*	*Electron configuration*	*Valence electrons*
6	C	He core, $2s^2\ 2p^2$	$2s^2 2p^2$
14	Si	Ne core, $3s^2\ 3p^2$	$3s^2 3p^2$
32	Ge	Ar core, $3d^{10}\ 4s^2 4p^2$	$4s^2 4p^2$
50	Sn	Kr core, $4d^{10}\ 5s^2 5p^2$	$5s^2 5p^2$
82	Pb	Xe core, $4f^{14} 5d^{10} 6s^2 6p^2$	$6s^2 6p^2$

Thus the outermost orbitals of each element from C to Pb contain s^2p^2 electrons. But the members of Group IVB elements— Ti, Zr and Hf have quite different electron arrangements as given in Table 19.2.

Table 19.2. Electronic structures of Group IVB elements.

At. No.	*Elements*	*Electron configuration*	*Valence electrons*
22	Ti	Ar core, $3d^2\ 4s^2$	$3d^2\ 4s^2$
40	Zr	Kr core, $4d^2\ 5s^2$	$4d^2\ 5s^2$
72	Hf	Xe core, $4f^{14}\ 5d^2\ 6s^2$	$5d^2 6s^2$

Thus the outermost orbitals in the titanium group of elements have s^2 electrons and the previous orbitals have the configurations $s^2p^6d^2$. In effect, the d level contains 2 electrons giving the valence shell electrons as d^2s^2. These arrangements are quite different from the carbon group elements and hence the chemistry is widely different, although the valence electrons remain 4 in both the groups but are of different types.

Before discussing the trends within the series and the gradation of the properties of sub-group IVA, a list of physical properties are given. This gives an idea regarding the comparative chemistry with respect to the treatment of the actual data.

The Physical Properties

Some of the important physical properties are given in Table 19.3 (a & b).

Table 19.3(a). Physical properties of Group IVA elements.

Properties	*C*	*Si*	*Ge*	*Sn*	*Pb*
Atomic No.	6	14	32	50	82
Atomic wt.	12.00	28.06	72.6	118.7	207.2
Outer electron orbitals	$2s^2\,2p^2$	$3s^2\,3p^2$	$4s^2\,4p^2$	$5s^2\,5p^2$	$6s^2\,6p^2$
Atomic radius (Å)	0.77	1.17	1.22	1.40	1.75
Ionic radius, M^{+4} (Å)	0.15	0.41	0.53	0.71	0.84
Ionization potential (ev) (M^+)	11.26	8.15	8.13	7.32	7.42
Density g/cm^3	3.50 2.25	2.33	5.36	7.31	11.34
Melting point °C	3600	1414	959	232	328
Boiling point °C	4830	2355	2700	2362	1755
Oxidation potential (v)	—	Si/Si^{+2} + 1.2	—	Sn/Sn^{+2} + 0.14	Pb/Pb^{+2} +0.12
Electronegativity	2.50	1.80	2.00	1.70	1.60

Table 19.3(b). Physical properties of Group IVB elements.

Properties	*Ti*	*Zr*	*Hf*
Atomic No.	22	40	72
Atomic wt.	47.90	91.20	178.60
Outer electron orbitals	$3d^24s^2$	$4d^25s^2$	$5d^26s^2$
Atomic radius (Å)	1.46	1.57	1.57
Ionic radius, M^{+4} (Å)	0.68	0.80	0.79
Ionization potential (ev) (M^+)	0.68	0.80	—
Density g/cm^3	4.50	6.40	11.40
Melting point °C	1800	1700	1700
Boiling point °C	3000	2900	3200
Oxidation potential (v)	Ti/Ti^{+4} + 1.0	Zr/Zr^{+4} +1.53	Hf/Hf^{+4} +1.70
Electronegativity	1.32	1.22	1.23

Group properties of IVA elements (Carbon Group) : The common properties are :-

(1) Except carbon and silicon, all other members are metals. The two representative elements, C and Si, predominate our environment since our animal and vegetable domains are made up primarily of compounds containing C—C bonds whereas the earth's crust and the minerals consist primarily of compounds containing Si—O bonds.

(2) Elementary Si, Ge and Sn have structures analogous to diamond (C) having crystal coordination number 4. The atom-to-atom bonds are covalent tetrahedral as in diamond. Pb is more metallic and has a cubic structure. The transition from purely covalent to metallic bonding is reflected in the sharp decrease in the m. p. from 3600°C for C to about 300°C for Pb. This decrease is attributed to the decrease in electrostatic attraction with the increase in size.

(3) The +4 oxidation states formed due to the removal of s^2p^2 electrons appear to be a characteristic property of this group. The +4 state is normally reflected in MO_2 but it is rather difficult to achieve an ionic state of +4. Even the ions Sn^{+4} and Pb^{+4} are not so common. But Sn^{+2} and Pb^{+2} are quite stable ions. As the atomic number increases from C to Pb having the outermost electrons s^2p^2, the two s electrons gradually become "inert pair" because of the stable state of $d^{10}s^2$ and do not take part in chemical bonding. Carbon and silicon do not have the inert s^2 pair of electrons. The decrease in the oxidation potentials of the system M^{+2} to M^{+4} also points to the same feature that among higher member the +4 state is rather difficult to achieve :

$Ge^{+2} \rightarrow GeO_2$ —	0.3 volt
$SnCl_4^{-2} \rightarrow SnCl_6^{-2}$ —	– 0.1 volt
$Pb^{+2} \rightarrow PbO_2$ —	– 1.5 volts

(4) Allotropic modifications are more prominent in the cases of C and Sn.

(5) Carbon is a unique element because of the remarkable property of combining with itself to form chains and rings (a process known as "catenation"). Silicon is also a unique element in so far as the formation of Si– O bonds is concerned. Pb is another unique member because it is the end product of the disintegration of many natural radio-elements.

(6) Si does not conduct electricity at normal temperature but at higher temperature its conductivity increases. This property is quite unlike metallic behaviour. Silicon is, therefore, called a semiconductor.

(7) Germanium is a scarce element and a semiconductor.

Comparison of Carbon Group (IVA) and Titanium Group (IVB)

(1) Elements of carbon group are non-transition elements whereas those of titanium group are transition elements with incomplete d level and show variable oxidation states in most of the compounds. The valence shell of carbon group contains s^2p^2 electron whereas the titanium group contains d^2s^2 electrons.

(2) The titanium group elements are tough metals and have very high melting and boiling points. Carbon group elements present a different picture, the melting point ranging from about 3600°C to about 300°C

(3) The oxides of carbon group elements are acidic although the acidic nature decreases from C to Pb. But the oxides of titanium group appear to be amphoteric. These characteristics are connected with the ionic sizes of the various atoms in the group.

Comparison of Carbon and Silicon : Because of the peculiar characteristics of C and Si, comparison of the chemistry of these two elements are made according to the points mentioned below :—

(1) Carbon and silicon are both elements of sub-group IVA and have s^2p^2 electrons in the outermost orbitals which govern their chemical behaviour almost in similar fashion. The difference arises due to the differences in atomic and ionic sizes which are important factors for the chemical properties.

C—$1s^2\ 2s^2\ 2p^2$ Si—$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

In Si the 3d orbitals are available for placement of electrons if needed.

(2) Carbon is abundantly found in nature both in the animal and vegetable kingdoms and also in carbonate minerals as well as in the free state as coal. Silicon is most abundant in silicate minerals and as silica and rocks. Thus C—C bonds give rise to a vast number of compounds whilst Si—O bonds produce a large number of silicate structures.

(3) The common oxides of C and Si are CO_2 and SiO_2 and although one is a gas and the other a tough solid both have acid properties producing H_2CO_3 and H_2SiO_3. The difference in properties is because CO_2 occur as isolated molecule whereas SiO_2 has polymeric molecule having 3-dimensional structure.

(4) C and Si form hydrides, halides and other similar compounds. Thus,

$$CCl_4 \quad SiCl_4 \quad CH_4 \quad SiH_4 \quad C_2H_6 \quad Si_2H_6$$

The properties of these compounds differ and the silicon compounds are easily hydrolysed because Si has tendency to form Si—O bonds. Hydrogen compounds of C are stable due to complete saturation of electron orbitals of C forming tetrahedral bonds.

(5) Carbon compounds exhibit the phenomenon of isomerism while it is not so pronounced in silicon compounds and, as a matter of fact, in all other elements this is a rare phenomenon.

(6) C has maximum covalency of 4 whereas in the case of Si it can expand to 6. This is because of the availability of d orbitals in the case of Si.

(7) In general, compounds of C are quite stable but most silicon compounds, except silicates and polymers, are unstable and are decomposed readily. Thus H_2CO_3 is stable in acids whereas H_2SiO_3 is decomposed to SiO_2.

Comparison of Silicon and Tin : Silicon has some resemblance with tin. In brief, the following points may be noted :—

(1) Both Si and Sn have s^2p^2 electron arrangement but the two s^2 electrons in Sn also act as *inert pair* giving Sn^{+2} and also Sn^{+4}, whereas Si is only tetravalent.

Si (14) — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

Sn (50)—$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^2$

(2) Si is non-metal whereas Sn is metallic.

(3) Both $SiCl_4$ and $SnCl_4$ are fuming liquids and are hydrolysed in water giving H_2SiO_3 and H_2SnO_3.

(4) Si-halides and Sn-halides have low melting and boiling points.

(5) SiH_4 and SnH_4 are formed easily and are gases.

(6) SiF_4 and SnF_4 give double flourides with alkali fluorides. Thus Na_2SiF_6 and Na_2SnF_6.

(7) Silicates and stannates are stable compounds. Meta-silicates and meta-stannates are more stable.

(8) Common salts of silicon, such as nitrates, sulphates etc. are not formed; but Sn gives such compounds.

(9) Sn gives more stable compounds of +2 states as $SnCl_2$ but Si does not.

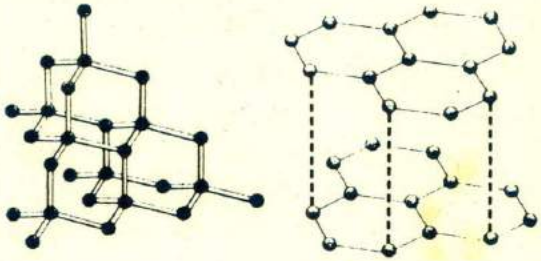
Inorganic Chemistry of Carbon

The bondings system in the atom of carbon has already been discussed earlier. The four equivalent bonds of carbon are homopolar in nature involving sp^3 hybrid orbitals and give rise to the enormous numbers of compounds, which are the basis of organic chemistry. Some compounds, such as oxides, carbides, cyanides, carbonyls etc. are, however, included in inorganic chemistry as a matter of custom.

Occurrence of carbon : (1) Carbon occurs free in nature in the form of diamond and graphite. (2) In the combined state it is found in natural gas, petroleum, coal, plants, animals and some minerals, such as limestone etc. (3) C is also found in air as CO_2. (4) In water it occurs as dissolved H_2CO_3, soluble carbonates and bicarbonates.

Graphite and Diamond : These are the two allotropic modifications of C and are giant molecules. Diamond contains the carbon atoms linked together in tetrahedral positions so that each carbon, in turn, is surrounded by four other carbon atoms (coordination No. 4) in a three-dimensional pattern. In effect, in diamond crystal each carbon uses sp^3 hybrid orbitals like that of CH_4 to produce a three-dimensional lattice. In graphite the polymer consists of sheets of carbon atoms, each sheet separated from the other by a distance of about 3.4 Å. The carbon atoms in the graphite may be regarded as fused systems of benzene rings, each carbon atom being surrounded by 3 other carbon atoms using sp^2 hybrid orbitals. In this system each C is bonded to the other two by single covalent bond and to third by double bond which is of the resonating type. Thus carbon

atoms are bonded in the graphite structure in the form of layers of hexagons. The illustration in Fig. 19—1 explains the two structures involving sp^3 and sp^2 bonding systems in diamond and graphite respectively.



Diamond

Crystal structure of diamond. Black spheres represent carbon held together by tetrahedral arrangement.

Graphite

Crystal structure of graphite. The layers of carbon held by weak valence bond (*van der Waal's* forces).

Fig. 19—1. Atomic arrangement of carbon in diamond and graphite.

Properties of Diamond and Graphite

Diamond is brittle but the hardest substance known. It is a good conductor of heat but not of electricity because of the electron saturated bonds. Diamond is transformed to graphite by heating at 1000°C. It is extremely inert to all chemicals at the ordinary conditions. Because the C—C bonds in diamond are very strong and extend throughout the crystal in three-dimensions, it is hard and has a high melting point of about 3600°C.

Graphite, also known as *Plumbago*, is a soft, grey solid having metallic lustre and slippery to touch. Graphite is a good conductor of electricity and is used as electrodes. The softness and electrical conductivity of graphite is in accordance with the structure. The layers in graphite are held together by van der Waals' forces and hence the slippery touch and softness of graphite. The graphite sheets in which C uses sp^2 bonding leaves one p orbital free to contribute to the mobile π electrons which is responsible for high electrical conductivity.

Graphite compounds are formed by the introduction of atoms or molecules between the layers of graphite structure. Such substances as $FeCl_3$, F_2, H_2SO_4,

K etc. have been introduced in between the layers giving rise to inclusion compounds or *clathrates*. The ill-defined graphitic acid, $C_{11}H_4O_5$, is formed when graphite is boiled with conc. HNO_3.

Charcoal, coke, carbon black and soot are amorphous or microcrystalline forms of carbon and are all of great industrial applications.

Diamond mostly comes from mines but quite recently synthetic diamond has been made by subjecting carbon under great pressure and high temperatures. Graphite is also mined but large quantities of graphite are made from amorphous carbon mixed with a little sand and Fe_2N_3 as catalyst and heating at about 3500°C in an electric furnace for a day or two. The carbon vapour condenses to produce graphite. This can also be made from petroleum, coke or anthracite coal as the starting material :

$$3C + SiO_2 = 2CO + SiC$$

SiC first formed is decomposed to give Si and C and silicon is volatilized away at that temperature leaving the graphite in the solid form :

$$SiC = Si + C$$

Graphite electrodes are mostly used in industrial electrolysis and also for making pencils. Large quantities of carbon are consumed in the manufacture of printing inks and hardening of automobile tyres. "Lamp black" which is actually used in tyres is made by the controlled combustion of methane in insufficient supply of oxygen to have the reaction :

$$CH_4 + O_2 = 2H_2O + C$$

Large quantities of carbon are also used for the extraction of metals.

Oxides of carbon

Carbon dioxide, CO_2 : This is the normal oxide of carbon and is obtained by various methods.

(1) By burning any form of carbon in excess of O_2 :

$$C + O_2 = CO_2 + 199 \text{ Kcal}$$

(2) By burning any compound of carbon in excess of O_2 :

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

$$C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O$$

(3) By strong heating of carbonate minerals, such as limestone, CO_2 is produced :

$$CaCO_3 = CaO + CO_2$$

(4) In the laboratory CO_2 is prepared by the action of dilute HCl on $CaCO_3$:

$$CaCO_3 + 2HCl = CO_2 + CaCl_2 + H_2O$$

(5) Fermentation process or decay of organic matter produces CO_2. Thus fermentation of glucose gives :

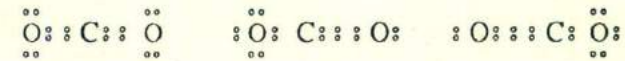
$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$$

(6) Commercially CO_2 is produced by burning coke in excess of air. The impure CO_2 containing N_2 and O_2 is passed under pressure through a cold dilute sodium carbonate solution which dissolves CO_2 but not N_2 and O_2. Pure CO_2 is obtained from the solution by just releasing the pressure :

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

Properties of CO_2 : It is a colourless, odourless gas and acidic in nature. It is appreciably absorbed in water and is readily liquefied. It freezes to a snow-like solid which sublimes without melting. This is the reason that solid CO_2 is known as "dry ice" and is a good refrigerant free from liquid. Freezing mixture of dry ice and an organic liquid, such as acetone, ether etc. produces very low temperature (– 77°C).

The electronic structure of CO_2 indicates that it is a linear molecule having the structures which show resonance :



$$C = C = O \qquad O — C \rightleftarrows O \qquad O \rightarrow C \rightarrow O$$

Due to resonance the bonds between C and O are strong and the molecule is quite stable towards heat. Burning Mg reduces CO_2 to pure C :

$$CO_2 + 2Mg = 2MgO + C$$

CO_2 is taken up by plants in presence of chlorophyll and sunlight synthesizing starch and other substances.

CO_2 dissolves in water to give H_2CO_3 which is a weak acid and most of its metallic salts are insoluble in water, particularly the heavy metals and alkaline earth carbonates. For this reason, these carbonates are found as minerals in nature. H_2CO_3 dissociates in water in two ways as a diprotic acid :

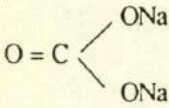
$$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{-2}$$

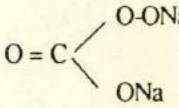
Metal carbonates

CO_2 dissolves in alkali solutions forming alkali carbonates, e. g., Na_2CO_3 and $NaHCO_3$. Bicarbonates of heavy metals or alkaline earth metals are readily soluble in water. The structure of carbonate has been discussed in the chapter on alkali metals. The low basicities of CO_3^{-2} and HCO_3^- do not permit formation of carbonates of those metals which are decidedly acidic. In other words, H_2CO_3 is not sufficiently acidic to form true carbonates with metal ions which are acidic. Thus Al^{+3}, Cr^{+3} and Fe^{+3} do not form true carbonates but give basic carbonates instead.

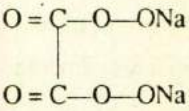
CO_2 when passed into a cold solution of Na_2O_2, the monopercarbonate, Na_2CO_4, is obtained. Dipercarbonate is made by electrolysis of cold saturated solution of, say, K_2CO_3. The relationships between the carbonates and percarbonates are shown below :



Sodium carbonate.



Sodium monopercarbonate



Sodium dipercarbonate (peroxalate)

Uses of CO_2 : (1) Manufacture of washing soda, $Na_2CO_3.10H_2O$ and baking soda, $NaHCO_3$, by Solvay process. (2) White lead, $2PbCO_3$, $Pb(OH)_2$, used as a pigment, (3) Soft drinks, (4) Fire extinguishers, (5) Dry ice used as refrigerant, (6) manufacture of urea.

Carbon monoxide, CO : Carbon monoxide is also a very familiar oxide of carbon and is of great technical importance. It is produced by various methods.

(1) By heating oxalic acid :

$$H_2C_2O_4 = H_2O + CO_2 + CO$$

CO_2 is absorbed in alkali solutions.

(2) By heating heavy metal oxides with carbon :

$$ZnO + C = Zn + CO$$

(3) By heating a carbonate with a metal :

$$MgCO_3 + Zn = ZnO + MgO + CO$$

(4) By passing CO_2 over C or Zn in the heated condition :

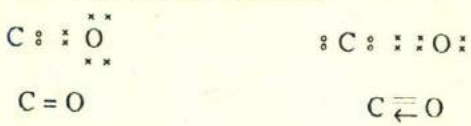
$$CO_2 + C = 2CO$$

$$CO_2 + Zn = ZnO + CO$$

(5) By reacting natural gas with steam in presence of a catalyst (NiO) :

$$CH_4 + H_2O \xrightarrow{NiO} CO + CO_2 + H_2$$

Properties and structure of CO : Carbon monoxide is a colourless, odourless gas, only slightly soluble in water. The structure of CO has been a puzzle and the best Lewis structure can be given by the following formulations representing resonances between the two forms :



$C = O$ $\qquad$ $C \rightleftarrows O$

Unlike CO_2, carbon monoxide is an active compound. CO burns in air to give CO_2 and heat energy. It reduces many metallic oxides to metals. Thus,

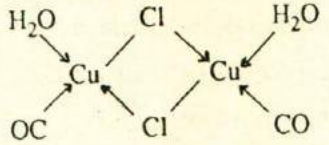
$$CuO + CO = Cu + CO_2$$

CO is, therefore, an important reducing agent in metallurgical operations. CO reacts with alkalies to produce formate :

$$CO + 2(OH^-) \rightleftharpoons H_2O + HCO_2^-$$

It combines with chlorine in presence of sunlight to give $COCl_2$ (carbonyl chloride, also known as phosgene). Phosgene is a poisonous gas. Another interesting property of CO is that it combines with many metals to form "metallic carbonyls". Thus Ni forms $Ni(CO)_4$, Fe gives $Fe(CO)_5$ and Co

produces $Co_2(CO)_8$. Both from industrial and structural points of view, the metallic carbonyls are very important and interesting compounds. CO is dissolved in cuprous chloride solution giving the compound :



Physiological action of CO : It is a highly toxic gas and combines with the hemoglobin of the blood to form a very stable compound destroying the ability of the blood to carry oxygen. CO inhalation causes paralysis of the respiratory organs. This danger of CO is particularly great in the exhaust gases of motor cars.

CO is not adsorbed by active charcoal but a mixture of CuO, MnO_2, Co_2O_3 and Ag_2O, known as *hopcalite*, oxidizes CO to CO_2 and is used in gas masks.

A filter paper moistened with $PdCl_2$ solution is turned pink, green or black due to the liberation of Pd in presence of CO. This is used as a test of CO.

Producer gas : When coke is heated in a limited supply of air, a mixture of CO and N_2 in the ratio of 1 to 3 by volume is formed. The product is known as *Producer gas*. It is used as a cheap fuel for many industrial works :

$$2C + 2O_2 = 2CO_2 + 54 \text{ Kcal}$$

$$CO_2 + C = 2CO - 39 \text{ Kcal}$$

Due to cooling down of the reaction for the second conversion, the temperature of the reaction is kept at 1100°C to effect the complete reduction of CO_2 to CO.

Water gas : When steam is passed over red-hot coke, a mixture of CO and H_2 is formed. This mixture is known as *Water gas* :

$$C + H_2O = H_2 + CO - 29 \text{ Kcal}$$

A high temperature (above 1000°C) is required to start the reaction. Since the reaction is endothermic the temperature soon falls below 1000°C when CO_2 begins to be produced :

$$C + 2H_2O = 2H_2 + CO_2 - 19 \text{ Kcal}$$

The final condition of equilibrium is represented by the reaction :

$$CO_2 + H_2 \rightleftharpoons H_2O + CO - 10 \text{ Kcal}$$

Thus at low temperatures, considerable amount of CO_2 is formed which lowers the calorific value of water gas. Hence devices have been developed to pass steam and air alternately over the bed of red-hot carbon to produce the mixture of $CO + H_2$ in the maximum proportions. When the steam is passed over the red-hot coke, it is called the "run period" or "cold blow"; but due to fall of temperature the passing of steam is stopped and hot air is blown to raise the temperature above 1000°C. This period is known as the "hot blow".

Water gas, known also as blue water gas, has a high calorific value. It is used as a fuel in industry and as a source of hydrogen and industrial alcohol (methyl alcohol) etc.

Carburetted water gas : When water gas is enriched with gaseous hydrocarbons obtained by cracking petroleum, the mixture is known as *carburetted water gas*. This contains mainly H_2, CO, saturated hydrocarbons and some CO_2 and N_2. This is also used as a fuel.

Semi-water gas : When a mixture of air and steam in the right proportions is passed over a bed of red-hot carbon the following reactions take place :

$$2C + 2O_2 = 2CO_2 + 54 \text{ Kcal}$$

$$C + H_2O = CO + H_2 - 29 \text{ Kcal}$$

Heat evolved by the combustion of carbon with oxygen present in air maintains the temperature of water gas reaction. The resulting gaseous mixture containing mainly CO, H_2 and CO_2, N_2 and some methane is called *Semi-water gas.*

Coal Gas

Coal gas is manufactured from coal by heating it in a closed vessel (retorts) in absence of air. The retorts are heated by producer gas (CO and air) to a temperature of about 1300°C. The operation of the coal gas producing plant is continuous and highly technical.

Purification of coal gas : The coal gas produced after carbonization of coal contains a number of impurities. They are mainly NH_3, H_2S, CS_2, HCN, besides naphthalene and tar. The tar condenses first in water condenser and also ammonia is separated as ammonical liquor.

The coal gas now enters the scrubber from the bottom. The scrubber is packed with coke and a fine spray of water slowly trickles downwards. Thereby all the residual NH_3, CO_2 and some H_2S and HCN are removed. The remaining gaseous impurities, such as CS_2, H_2S, and HCN are removed by passing through purifiers containing lime and iron hydroxide. The complicated reaction takes place and may be represented by some of the equations given below. H_2S must always be removed since it produces undesirable products and lowers the calorific value of the coal gas :

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

$$Ca(OH)_2 + 2H_2S \longrightarrow Ca(HS)_2 + 2H_2$$

$$Ca(HS)_2 + CS_2 \longrightarrow \underset{\text{(Calcium thiocarbonate)}}{CaCS_3} + H_2S$$

$$2Fe(OH)_3 + 3H_2S \longrightarrow Fe_2S_3 + 6H_2O$$

$$Fe_2S_3 + HCN \longrightarrow Fe_4[Fe(CN)_6]_3$$

$$NH_3 + HCN \longrightarrow NH_4CN + H_2S \longrightarrow NH_4CNS$$

Coal gas is a mixture of gases containing the following :

CH_4— 30%, C_2H_4—4%, C_2H_2—1%

H_2—50%, CO—10%, N_2—5%

Uses of coal gas : (1) Gaseous fuel. (ii) For providing inert atmosphere. (iii) For providing reducing atmosphere in metallurgy. (iv) Smelting.

Coke is used as a fuel and reducing agent in metallurgy.

Coal tar is used for extracting a vast number of organic substances.

Carbon disulphide, CS_2 : Carbon is oxidized by elementary sulphur to CS_2 at the temperature of electric arc in absence of air. High temperature is required because of the endothermic reaction :

$$C + 2S = CS_2 - 19 \text{ Kcal}$$

CS_2 is also produced commercially by burning methane in sulphur vapour at about 700°C in presence of silica gel or activated Al_2O_3.

The CS_2 obtained in the vapour state is condensed to liquid and purified by shaking the liquid with Hg and distilling over P_2O_5. CS_2 is a colourless liquid with a characteristic smell and boils at 46°C.

It is poisonous and a highly inflammable liquid. It ignites in air forming SO_2 and CO_2. It explodes in air or NO :

$$2CS_2 + 5O_2 = 2CO + 4SO_2$$

$$2CO + O_2 = 2CO_2$$

Thiocarbonates are formed when CS_2 reacts with Na_2S or with NaOH :

$$CS_2 + Na_2S = Na_2CS_3$$

$$3CS_2 + 6NaOH = Na_2CO_3 + 2Na_2CS_3 + 3H_2O$$

Similarly,

$$3CS_2 + 6NH_4OH\ (conc) = 2(NH_4)_2CS_3 + (NH_4)_2CO_3 + 3H_2O$$

Thiocarbonic acid, H_2CS_3 : This is obtained when sodium or ammonium thiocarbonate, $(NH_4)_2CS_3$, is added to excess of conc. HCl. This is a bright red liquid :

$$(NH_4)_2CS_3 + 2HCl = H_2CS_3 + 2NH_4Cl$$

Thiocarbonyl chloride is formed when CS_2 reacts with PCl_5 :

$$PCl_5 + CS_2 \longrightarrow S = C\begin{matrix}Cl\\Cl\end{matrix} + PSCl_3$$

CS_2 is a good solvent for oils, fats, sulphur, phosphorus, iodine, rubber etc. It is used in making rayon, cellophane and CCl_4. When Cl_2 is passed into CS_2 containing iodine or $SbCl_5$ (catalyst), CCl_4 is obtained. The process is used for the manufacture of CCl_4 :

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2$$

Metal Carbides : Carbon combines with many metals to produce carbides. These are produced either by the direct reaction of metals with carbon or

by heating the oxide of the metal with carbon at high temperatures. Some of these carbides have very high melting points, such as, TaC—4400°C. Thus,

$$2Li + 2C \rightarrow Li_2C_2$$

$$4Al + 3C \rightarrow Al_4C_3$$

$$BaO + 3C \rightarrow BaC_2 + CO$$

Most of the metal carbides with water give C_2H_2 by hydrolysis of C_2^{-2} ion :

$$Na_2C_2 + 2H_2O \rightarrow NaOH + C_2H_2$$

Only Al_4C_3 and Be_2C give CH_4 on hydrolysis with H_2O :

$$Be_2C + H_2O \rightarrow Be(OH)_2 + CH_4$$

Calcium carbide, CaC_2, is an important commercial product. CaC_2 is manufactured by heating CaO and coke in an electric arc furnace :

$$CaO + 3C = CaC_2 + CO$$

CaC_2 is an ionic compound containing Ca^{+2} and C_2^{-2} ions. It is hydrolysed in water readily giving acetylene, C_2H_2, which is the starting material of a very large number of products :

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

CaC_2 is also used to make calcium cyanamide, $CaCN_2$.

Calcium cyanamide, $CaCN_2$: When nitrogen (air) is passed over CaC_2 mixed with some $CaCl_2$ at a temperature of about 1100°C, N_2 is taken up by CaC_2 forming $CaCN_2$ and liberating C :

$$CaC_2 + N_2 = CaCN_2 + C$$

The mixture $CaCN_2$ and C is known as Nitrolime and is used as a fertilizer and for production of NH_3 by the hydrolysis of $CaCN_2$:

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

Cyanogen, C_2N_2 : This colourless gas is obtained by various methods : (1) Cyanides of Ag, Au and Hg give C_2N_2 :

$$2AgCN \rightarrow 2Ag + C_2N_2$$

(2) When $Hg(CN)_2$ is heated with $HgCl_2$. Thus,

$$Hg(CN)_2 + HgCl_2 \rightarrow C_2N_2 + Hg_2Cl_2$$

(3) When $CuSO_4$ solution is treated with KCN, C_2N_2 is evolved. The method is analogous to the liberation of I_2 from KI when it is added to $CuSO_4$ solution :

$$2CuSO_4 + 4KCN = 2K_2SO_4 + 2CuCN + C_2N_2$$

Cyanogen is a poisonous gas, burns with blue flame and it is hydrolysed by water :

$$C_2N_2 + H_2O = HOCN + HCN$$

With KOH it gives KCN and KCNO :

$$C_2N_2 + 2KOH = KCN + KCNO + H_2O$$

In acid aqueous solution C_2N_2 gives oxamide :

$$C_2N_2 + H_2O \longrightarrow (CONH_2)_2$$

C_2N_2 on reduction with hydrogen gives $NH_2—CH_2—CH_2—NH_2$ (ethylene diamine). Hence, C_2N_2 has a linear structure.

$$N \equiv C—C \equiv N$$

or

$$:\!N\!:\!:\!:C:C:\!:\!:N\!:$$

Hydrogen cyanide, HCN : This poisonous, almond smelling gas is formed when a cyanide is heated with an acid :

$$NaCN + HCl = NaCl + HCN$$

HCN in water solution gives a weak acid, hydrocyanic acid. The alkali metal salts of this weak acid in aqueous solution are alkaline by hydrolysis :

$$HCN + H_2O \rightarrow H_3O^+ + CN^-$$
$$CN^- + H_2O \rightarrow HCN + OH^-$$

HCN is a poisonous substance, 0.05 g. is sufficient to kill a man because it easily combines with iron in the blood and enzymes, CN^- ion has all the properties of halide ions and hence C_2N_2 is sometimes referred to as *pseudohalogen*. HCN has the following structure :

$$H—C \equiv N$$

Cyanates, CNO^- : When C_2N_2 is passed through alkali solutions, it gives cyanates and cyanides, just as chlorine gives hypochloride and chloride :

$$C_2N_2 + 2NaOH = NaCNO + NaCN + H_2O$$

KCNO is formed when KCN is heated with PbO or MnO_2 :

$$KCN + PbO = KCNO + Pb$$

HCNO is unstable and is decomposed by water to NH_3 and CO_2 :

$$NaCNO + HCl = HCNO + NaCl$$

$$\downarrow +H_2O$$

$$NH_3 + CO_2$$

Concentrated solution of NH_4Cl gives NH_4CNO with KCNO :

$$KCNO + NH_4Cl = NH_4CNO + KCl$$

NH_4CNO, on heating, gives urea, $NH_2—CO—NH_2$.

Thiocyanates, CNS^- : These are obtained when a cyanide is melted with S. Thus,

$$KCN + S = KCNS$$

When $(NH_4)_2S$ is treated with HCN, ammonium thiocyanate is obtained :

$$(NH_4)_2S + HCN \rightarrow NH_4CNS + NH_4SH$$

Free HCNS is obtained by treating $Ba(CNS)_2$ with dil. H_2SO_4 :

$$Ba(CNS)_2 + H_2SO_4 = BaSO_4 + 2HCNS$$

With ferric salt solutions thiocyanates give the blood-red colour which is a familiar test for Fe^{+3} ion :

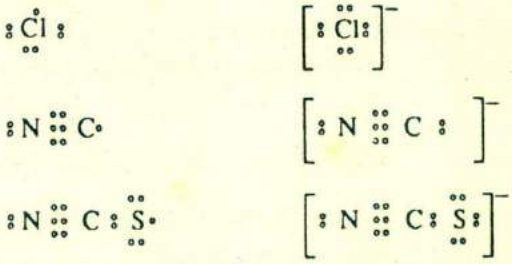
$$3NH_4CNS + FeCl_3 = Fe(CNS)_3 + 3NH_4Cl$$

It will be interesting to note that CO_2, cyanate CNO^- and cyanamide CN_2^{-2}, are isoelectronic and have similar structures :

$O = C = O$ $\quad$ $[O = C = N]^-$ $\quad$ $[N = C = N]^{-2}$

The ions are easily hydrolysed to give CO_2 and NH_4^+ ion.

The relationship between the structures of Cl^-, CN^- and CNS^- ions may be illustrated as follows :



SILICON

Organic substances containing C—C bonds are dominant in animal and vegetable worlds. Substances containing Si—O—Si bonds are of great importance in the mineral world. The earth's crust is primarily made of clay and silicate minerals which have Si—O—Si bonds arranged in chains, layers and network having SiO_4 tetrahedron as the unit of structure.

Occurrence : Silicon is never found in the free state. SiO_2 and various compounds known as silicates constitute about 86% of the earth's crust. Silicon is about 26%. Silicon is, therefore, next to oxygen in abundance. Silica, SiO_2, occurs in many forms, such as sand, sandstone, quartz, agate, flint etc. The various silicate minerals have been described in their proper places.

Preparation of Silicon : Silicon has been prepared both in the crystalline and amorphous forms. Both the forms appear to have the same atomic arrangement in the crystals and have somewhat diamond-like structures. Each silicon is covalently bonded to four adjacent silicon atoms at the corners of regular tetrahedron and this is extended in three dimensional network giving a giant molecule. Silicon is, therefore, hard and brittle.

Silicon is obtained when $SiCl_4$ is reduced by sodium :

$$SiCl_4 + 4Na = Si + 4NaCl$$

By the action of magnesium on SiO_2 at high temperature, amorphous silicon is obtained :

$$SiO_2 + 2Mg = Si + 2MgO$$

In this reaction some magnesium silicide is also formed :

$$SiO_2 + 4Mg = Mg_2Si + 2MgO$$

The Mg_2Si and MgO are dissolved in HCl giving amorphous brown powder of silicon. Crystalline silicon is obtained by heating K_2SiF_6 with Al in iron tubes :

$$3K_2SiF_6 + 4Al = 6KF + 4AlF_3 + 3Si$$

K_2SiF_6 when heated with Zn and the product dissolved in HCl, needle-shaped crystalline adamantine silicon is obtained :

$$K_2SiF_6 + 2Zn = 2KF + 2ZnF_2 + Si$$

Uses of Si : (1) For making acid resisting steels. (2) Making ferrosilicon, a strong reducing agent. (3) Pure silicon is used as transistors and microchips in electronics.

Some Important Compounds of Silicon

Silicon hydrides : Silicon forms a series of hydrides as in the case of carbon but only in limited number. Some of these are SiH_4, Si_2H_6, Si_3H_8, Si_4H_{10}, Si_5H_{12} and Si_6H_{14}. The chemical properties of these silicon hydrides are quite different from those of the hydrocarbons.

SiH_4, silane or silicomethane, is prepared when Mg_2Si reacts with dil. HCl :

$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$$

SiH_4 is also obtained when $SiCl_4$ is reduced with $LiAlH_4$ in ether solution :

$$SiCl_4 + LiAlH_4 = SiH_4 + LiCl + AlCl_3$$

Si_2H_6, disilane (silicoethane) is obtained by treating lithium silicide with HCl :

$$Li_6Si_2 + 6HCl = 6LiCl + Si_2H_6$$

SiH_4 is a colourless gas and Si_2H_6 is a colourless liquid. All the silanes are spontaneously inflammable in air forming SiO_2 and water :

$$SiH_4 + 2O_2 = SiO_2 + 2H_2O$$

Silanes are easily hydrolysed forming SiO_2 and H_2. Alkali solutions give the alkali silicates, M_2SiO_3 and H_2 and all silanes are very sensitive to the reactions with alkalies.

The reactivity of silanes as compared to the hydrocarbons is the weakness of Si—H and Si—Si bonds. H_2O or O_2 is easily accommodated by Si atom because of the expansion of the coordination number due to the availability of d orbitals in Si atom.

Silicon compounds having the corresponding formula of carbon compounds are also known, such as, silicochloroform, $SiHCl_3$, obtained by stepwise halogenation of silane by HCl in presence of $AlCl_3$ as a catalyst :

$$SiH_4 + HCl \xrightarrow{AlCl_3} SiH_3Cl + H_2$$

$$SiH_3Cl + HCl \longrightarrow SiH_2Cl_2 + H_2$$

$$SiH_2Cl_2 + HCl \longrightarrow SiHCl_3 + H_2$$

$$SiHCl_3 + HCl \longrightarrow SiCl_4 + H_2$$

Silicon halides : Silicon gives tetrahalides, SiX_4, and also some mixed halides, such as $SiCl_2F_2$.

Silicon tetrachloride : $SiCl_4$ can be prepared by direct chlorination of silicon at high temperature or by direct chlorination of a mixture of SiO_2 and carbon :

$$Si + 2Cl_2 = SiCl_4$$

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$$

$SiCl_4$ is a colourless liquid, boiling point 58°C. This produces dense fumes in moist air due to the formation of finely divided silicic acid in moist air :

$$SiCl_4 + 4H_2O = H_4SiO_4 + 4HCl$$

During war the smoke screen is produced by liberating NH_3 and $SiCl_4$ at the same time. The density of the smoke is increased due to the formation of solid NH_4Cl.

$SiCl_4$ is readily attacked by H_2O, but CCl_4 is not.

Silicon tetrafluoride, SiF_4, is made by spontaneous burning of silicon in fluorine or by the action of HF on SiO_2 or a silicate :

$$Si + 2F_2 = SiF_4$$

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

$$CaSiO_2 + 6HF = CaF_2 + SiF_4 + 3H_2O$$

SiF_4 is a gas and is hydrolysed in water forming hydrofluorosilicic acid as well as orthosilicic acid :

$$3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6$$

Fluorosilicic acid is also obtained by the action of HF on sand :

$$SiO_2 + 6HF = H_2SiF_6 + 2H_2O$$

Fluorosilicic acid is a stronger acid than sulphuric acid and it is a fuming liquid. On evaporation it breaks up to produce HF and SiF_4 :

$$H_2SiF_6 = 2HF + SiF_4$$

Hydrolysis of SiX_4 or the group IV metal halides, MX_4, in general proceeds in two manners :—

(1) Simple hydrolysis gives HX and $M(OH)_4$ or MO_2 :

$$SiF_4 + 4H_2O = Si(OH)_4 + 4HF$$

This occurs if the ratio of covalent radii $\frac{rM}{rX}$ is small (1.2).

(M = metal, X = halogen)

(2) When the ratio of covalent radii, $\frac{rM}{rX}$, is larger than 1.2, then the hydrolysis becomes complex forming complex ion, such as $[MX_n(H_2O)_{6-n}]^{4-n}$ and ultimately forming H_3O^+ ion and their conjugate bases. The acidity of the solution is increased. Some of the complex ions are SiF_6^{-2}, $SnBr_2(H_2O)_4^{+2}$.

Silicic acids and silica gel : When a strong mineral acid is added to a solution of an alkali metal silicate, this results in the formation of orthosilicic acid :

$$Na_4SiO_4 + 4HCl = H_4SiO_4 + 4NaCl$$

H_4SiO_4 remains in a colloidal solution but after some time it is precipitated out as a gelatinous mass. A mixture of sodium silicate and ammonium chloride also gives the colloidal solution or a gelatinous precipitate. The gelatinous mass is separated from other ions by dialysis.

Orthosilicic acid on stepwise dehydration by heating gives metasilicic acid, H_2SiO_3, disilicic acid, $H_6Si_2O_7$, and "trisilicic acid". On complete dehydration, SiO_2 is formed.

Silica gel is obtained by the dehydration of silicic acid to form silica containing a very small percentage of moisture. The silica gel has open and porous structure with large surface area and is used for absorption of gases and moisture and as a catalyst in chemical reaction.

Silicon carbide, SiC (Carborundum) : This is obtained on a large scale by heating a mixture of sand and coke in an electric furnace at a temperature of about 2000°C :

$$SiO_2 + 3C = SiC + 2CO$$

Carborundum is a blue black iridescent crystal as hard as diamond and exists in three different crystalline forms having C and Si at alternate positions in the crystal network so that each atom is surrounded tetrahedrally by four others. This accounts for the inactivity, hardness and thermal stability of SiC. It is used as abrasive for polishing, grinding and cutting.

SiC is attacked by fused alkali to give Na_2SiO_4 and Na_2CO_3.

Silicon dioxide, SiO_2 : Silica occurs in nature as sand and quartz. There are three well-defined crystalline forms of silica :

$$\alpha \text{ quartz} \overset{573°C}{\rightleftharpoons} \beta \text{ quartz} \overset{870°C}{\rightleftharpoons} \text{tridymite} \overset{1500°C}{\rightleftharpoons} \text{crystobalite}$$

Crystobalite has a diamond structure having linear Si—O—Si bonds but in quartz and tridymite Si—O—Si bonds are non-linear.

A section of symmetrical arrangement of atoms is β-quartz is shown in Fig. 19—2 showing the plane of the hexagonal pattern.

SiO_2 is hard, refractory, brittle and colourless solid. CO_2 is a gas at ordinary temperature having separate molecules and even in dry ice CO_2 molecules have

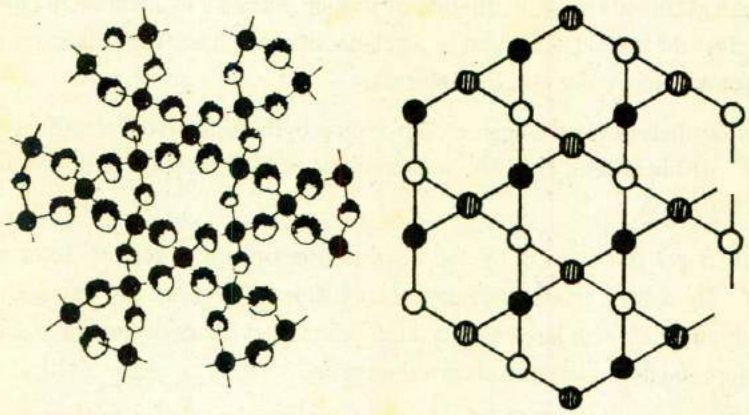


Fig. 19—2. Projection of silicon atom in β-quartz. The silicon atoms lie in three different planes shown by the black circles, shaded circles and empty circles giving a hexagonal pattern.

little intermolecular attractions. Each C in dry ice (CO_2) is linked to two O atoms by double bonds, whereas in SiO_2 each Si is attached to four O atoms by single bonds in tetrahedral forms which are again linked together in three dimensional pattern by sharing oxygen atoms at the corners between two tetrahedra forming a giant molecule having Si—O—Si non-linear bonds. The overall ratio of Si to O is 1: 2 as in SiO_2.

By melting quartz at 1600°C, silica glass is produced which is transparent to visible and ultraviolet light and is used in optical instruments.

SiO_2 is an stable compound and is reduced by only very reactive metal. It is not attacked by acid except by HF.

Ferrosilicon, FeSi : When silicate iron ore is reduced in electric furnace, ferrosilicon is formed. It is used in steel industry to make acid-resistant steel, e. g., "duriron" and steel of high magnetic properties. Silicon also acts as de-oxidizing agent in steel.

Hydrogenite : A mixture of ferrosilicon and solid NaOH liberates H_2 gas with water and is known as hydrogenite.

Water glass, Na_2SiO_3 : When silica is fused with Na_2CO_3 or NaOH, sodium silicate, Na_2SiO_3, is formed :

$$2NaOH + SiO_2 = Na_2SiO_3 + H_2O$$
$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

The product is a glassy mass soluble in water giving a thick viscous liquid which is called "water glass". It is a commercial product and actually does not conform to the simple formula of Na_2SiO_3 but contains excess SiO_2 in the form of $Na_6Si_3O_9$, $Na_4Si_3O_8$ etc. Water glass is used in making soap, washing compounds, fire proofing, adhesive and for egg preservation. Na_2SiO_3 on hydrolysis gives alkaline reaction because NaOH formed is a stronger base :

$$Na_2SiO_3 + 2H_2O = H_2SiO_3 + 2NaOH$$

Glass : Glass is a complex mixture of silicates and is actually a supercooled liquid. It is transparent, brittle and has no orderly arrangements of atoms as in crystals but has random distributions of the atoms. It does not melt on heating at a particular temperature but gradually becomes soft. Colour of the glasses are due to the presence of foreign metal either present in the raw material or deliberately added.

Raw materials for glasses : These vary from type to type and the following are the important raw materials used :—

(a) *Silica, SiO_2 :* Small quantity of Al_2O_3 does not produce any harmful effect but Fe_2O_3 colours the glass and is generally removed.

(b) *Boric oxide, B_2O_3:* This is added in the form of H_3BO_3 or borax only in borosilicate glasses which have low co-efficient of expansion.

(c) P_2O_5 or As_2O_3 is added when opalescent glasses are to be produced.

(d) Li_2O, K_2CO_3, CaO, Na_2CO_3, $BaCO_3$, MgO, PbO_4, ZnO and $CaCO_3$ are used as basic oxides to produce the glasses. These different basic oxides produce different types of glasses, such as,

(i) Soft glass contains Na and Ca silicate.

(ii) Hard glass contains K and Ca silicate and fuses at high temperature.

(iii) Flint glass contains K and Pb silicate for optical instruments.

(iv) Bottle glass is a soda-lime glass without removal of ferrous silicate.

(v) *Jena glass:* Zn and Ba-borosilicate glass.

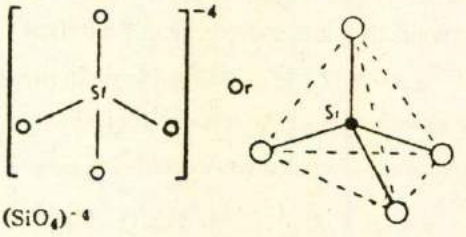
(vi) *Pyrex glass :* Barium borosilicate glass having low co-efficient of expansion.

(e) *Colouring matter for glass:* Certain metallic oxides are added to glass for the purpose of colouring the glass. For instance, ferrous iron gives green colour whereas ferric iron imparts yellow colour. Cobalt oxide gives intense blue colour, carbon gives amber colour and so on.

The chemical reactions between the ingradients are of very complex nature and no definite compounds are formed. Soft glass consists of sodium-calcium silicates. Glasses manufactured by any of the above ingradients are subjected to annealing, i.e., the process of slow cooling in order to avoid sudden cracking down to pieces.

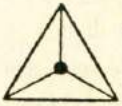
Natural silicates : These are silicate minerals occurring in nature and are of varied chemical compositions and structures. However, a systematic study of the silicate minerals have been made and it has been found that all of them have the same basic structures of SiO_4 tetrahedron joined together in various manners. Each Si atom is at the centre of a tetrahedron with 4 oxygen atoms at the corners. These minerals have been classified on the basis of the linking of Si-O tetrahedra. Thus :-

1. Single SiO_4 tetrahedron has an independent group in the crystal lattice. Thus olivine, Mg_2SiO_4, and zircon, $ZrSiO_4$, have individual SiO_4 tetrahedra bound together by Mg^{+2} or Zr^{+4} ions :



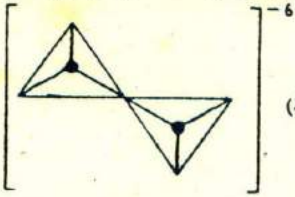
$(SiO_4)^{-4}$ $(SiO_4)^{-4}$

Or more simply as,



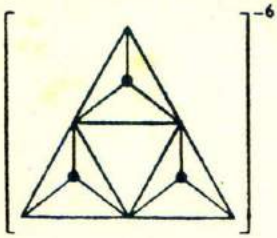
$(SiO_4)^{-4}$ tetrahedron. The black circle indicates Si atom at the centre. 4 oxygen atoms are situated at the 4 corners of the tetrahedron.

2. Two SiO_4 tetrahedra may share one corner forming Si_2O_7 group. Thus in hemimorphite, $Zn_4(OH)_2Si_2O_7$, and $Sc_2Si_2O_7$, we have,

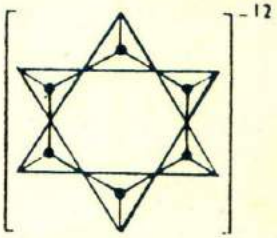


$(Si_2O_7)^{-6}$ anion

3. Three or six SiO_4 tetrahedra may share corners and form a closed ring as in $Ca_3Si_3O_9$ and benitoite, $BaTiSi_3O_9$, and beryl, $Be_3Al_2Si_6O_{18}$ respectively :

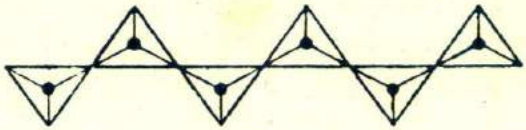


$(Si_3O_9)^{-6}$



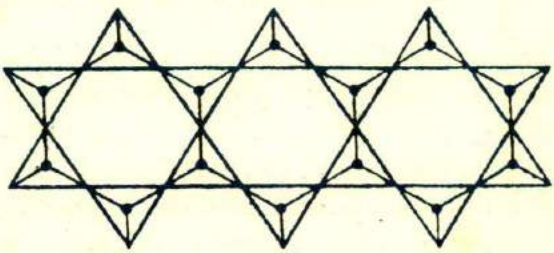
$(Si_6O_{18})^{-12}$

4. Linking of endless chain of SiO_4 tetrahedra by sharing two O atoms as in diopside, $CaMg(SiO_3)_2$, and pyroxenes, $[MgSiO_3]n$:



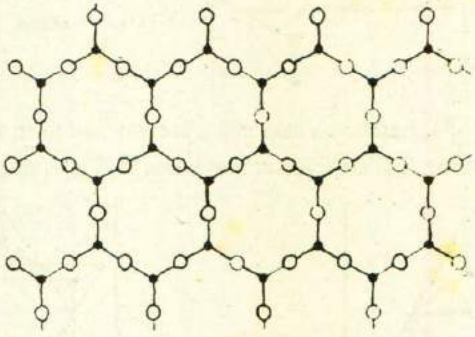
$(SiO_3)_n^{-2n}$ anion

5. Linking of SiO_4 tetrahedra to give double Si—O chains as in the fibrous asbestos and tremolite, $Ca_2Mg_4(Si_4O_{11})_2.Mg(OH)_2$:



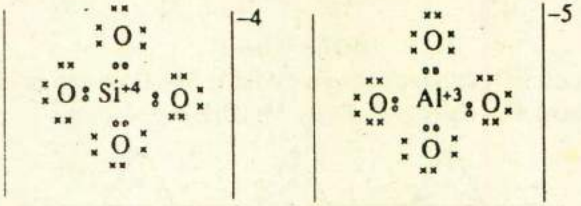
$(Si_4O_{11})_n^{-6n}$ anion

6. Linking of SiO_4 tetrahedra giving extended double chain to form sheets as in the case of talc, $Mg_3Si_4O_{10}(OH)_2$, and mica, $KAl_2AlSi_3O_{10}(OHF)_2$:



$(Si_2O_5)_n^{-2n}$ anion

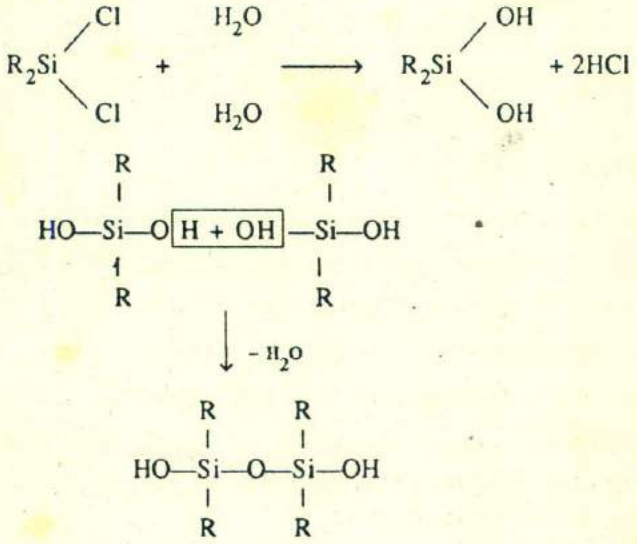
7. Linking of SiO_4 tetrahedra giving three dimensional Si—O network in which some Si^{+4} has been replaced by Al^{+3}. The excess negative charge is neutralized by introduction of a positive ion throughout the network as in feldspar, $KAl(Si_3O_8)$ or zeolites, $Na_2Al_2Si_3O_{10}.H_2O$. Aluminium ion, Al^{+3} replaces Si^{+4} because of the similar size of the two ions (about 0.50 Å).



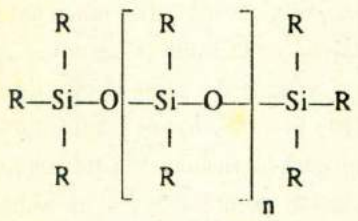
Zeolite, therefore, contains Na^{+2} or K^+ ion in order to balance the electrical charges and the structure is such that Na^+ or K^+ ions can be dislodged by Ca^{+2} ion because of similar size without changing the basic structure of the silicate. This phenomenon in natural silicates is known as *isomorphous displacement*. Zeolite, therefore, functions as a base exchanger and is used in water purification, although now-a-days synthetic base exchangers are being extensively used.

Silicones : The production of organosilicon polymers has been a recent development in the field of silicon chemistry. The organosilicon polymers are generally known as *Silicones* and have been of great industrial use. They are stable towards heat and chemical reagents and repel water. Depending upon polymerization complexity, the silicones may be in the form of oily liquids, greases, rubber-like substances or resins. They find their use as lubricating oils, electrical insulators, water proofing etc. Silicones lubricating oils are employed where great variations of temperature do not permit the use of ordinary lubricants. Water repellent films are coated on paper, silk, glass, fabrics. etc. by simply exposing the materials to the vapour of trimethyl chlorosilane, $(CH_3)_3SiCl$. The thin film consists of $(CH_3)_2Si{-}O$ groups which repels water.

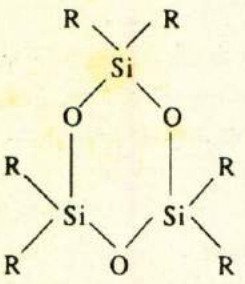
Some of the polymeric forms of the silicone polymers are made from organochlorosilanes of the types R_2SiCl_2 by hydrolysis. R may be CH_3, C_2H_5, C_6H_5 or other radicals. The hydrolysis is followed by polymerization (condensation reaction) through the elimination of H_2O from two adjacent OH groups of $R_2Si(OH)_2$:



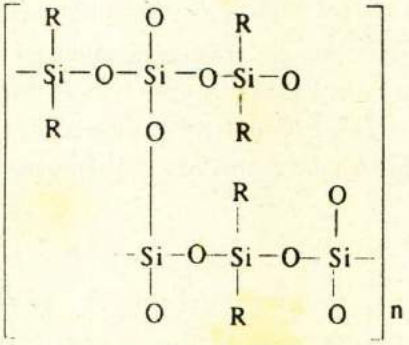
There are linear, cyclic and cross-linked types of silicone polymers as shown below :



linear silicone



cyclic silicone



cross-linked silicone

GERMANIUM

Mendeleef predicted the existence of this element and named it EKA-silicon.

Germanium is rare and occurs in argysodite, Ag_4SeS_4, and in some sulphide ores. It also occurs in coal ash along with other metals.

GeO_2 when reduced with C or H_2 gives the metal Ge.

Also the reaction, $GeBr_4 + 4Na \rightarrow Ge + 4NaBr$ gives Ge.

Ge metal retains its lustre in air like Sn. It is not affected by HCl, H_2SO_4 (dil.), but dissolve in HNO_3 and in dil. NaOH only slightly. Fused alkalies dissolve it completely forming Na_2GeO_3.

Germanium does not form allotropes and occurs only in diamond structure but it is opaque and gray in colour.

Ge forms both Ge^{+2} and Ge^{+4} compounds. Ge^{+2} is easily oxidized to Ge^{+4} or reduced to Ge. GeO and GeO_2 are amphoteric. $GeCl_4$ resembles $SiCl_4$ and Ge forms hydrides GeH_4, Ge_2H_6, Ge_3H_8 and other organometallic compounds.

When Ge is alloyed with other elements, it has the unique property of allowing an electric current to pass in only one direction. The rectifying capacity of metallic Ge crystals has been used in radar and as transistors for amplifying small currents of electricity as a substitute for vacuum tubes or thermionic valves. Germanium belongs to the semiconductor group of elements. It shows increased electrical conductivity at higher temperatures.

TIN

Sn has the electronic configuration :

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^2$$

This aspect of the electron arrangement is reflected in the properties of Sn and its compounds, particularly with regard to the oxidation states of Sn. Since $4d^{10}\ 5s^2$ electron arrangement represents stable configuration, the outermost $5s^2$ electrons in Sn do not normally show much activity and hence are known as *inert pair* of electrons. Thus Sn^{+2} state is more stable than Sn^{+4}.

Sources of Tin

(1) Cassiterite (Tinstone)—SnO_2.

(2) Various pyrites of Fe, Cu and Zn contain small quantity of Sn.

Metallurgy

1. Concentration of ore is generally done by washing the tinstone in a stream of water. Tinstone fragments being heavier are left at the bottom.

2. The tinstone is then roasted to remove arsenic and sulphur as volatile oxides. The volatile As_2O_3, is actually collected. The oxides of other metals are also formed during roasting.

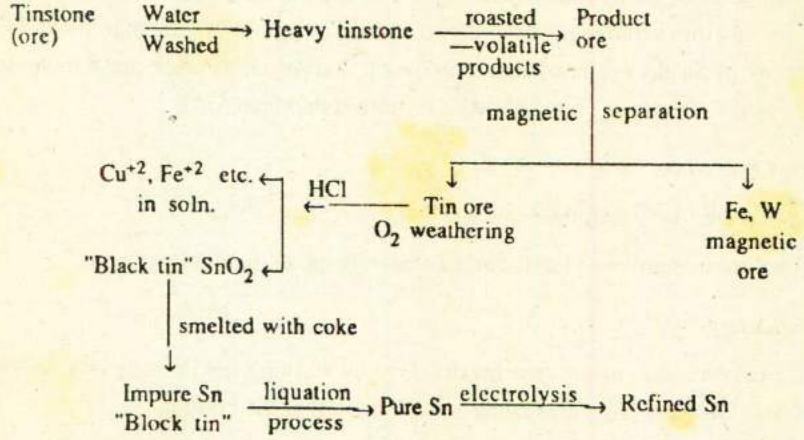
3. Roasted tinstone contains iron and manganese tungstate because $FeWO_4$ occurs in cassiterite. These are separated from tinstone by magnetic separation because both Fe and Mn tungstate are magnetic in nature. Travelling belt with

electromagnetic roller separates the magnetic and non-magnetic parts into two heaps.

4. The roasted tinstone is then treated with hydrochloric acid to dissolve out CuO and Fe_2O_3. Alternately, the roasted tinstone is allowed to stand in a heap in moist condition and then leached with water to dissolve out $CuSO_4$ and $FeSO_4$ formed. The concentrated tinoxide is known as *black tin.*

5. The purified SnO_2 is mixed with coke and smelted in a reverberatory furnace with a little lime as flux to form $CaSiO_3$ with SiO_2. The molten tin which collects on the bottom of the furnace is drawn off and cast into blocks known as *block tin*,

6. The refining of the crude tin is done by *liquation process.* The tin blocks are remelted and allowed to flow away from the higher melting impurities. This may further be purified by electrolysis. As usual, the impure tin is made the anode while the pure tin is cathode and the bath consists of H_2SiF_6 and H_2SO_4.



In small scale it may be obtained by treating $SnCl_2$ with zinc metal :

$$SnCl_2 + Zn \rightarrow Sn + ZnCl_2$$

Properties of Tin

Physical properties : Tin exists in three solid allotropic forms : (a) Gray tin having cubic structure; (b) White tin which is malleable and having

tetragonal structure ; (c) Brittle tin having rhombic structure. The three forms are interconvertable :

$$\text{Gray tin} \overset{13^\circ C}{\rightleftharpoons} \text{White tin} \overset{170^\circ C}{\rightleftharpoons} \text{Brittle tin}$$

Malleable tin is silvery white and when a rod of it is bent or hit with a hammer, it produces a sound described as *tin cry* due to the fact that the crystals slip over one another. Zn and Cd behave similarly. White tin at low temperature (in cold countries where temperature falls below 0°C) automatically changes to gray tin which is a white powder. The change progresses slowly originating from a spot of the tin articles and spreads over the entire area as happens in the case of infection in a plant or animal body. For this reason, it is known as *tin disease* or *tin pest*.

Chemical properties : The chemical properties have been described in the general properties of group IV elements. Sn is a stable metal and is converted to SnO_2 only on heating to above 1500°C. Tin dissolves in HCl giving $SnCl_2$ and evolving H_2. Conc. H_2SO_4 gives $Sn(SO_4)_2$ but dil. H_2SO_4 gives $SnSO_4$:

$$Sn + H_2SO_4 = SnSO_4 + H_2$$

$$Sn + 4H_2SO_4 = Sn(SO_4)_2 + 2SO_2 + 4H_2O$$

It is also dissolved in dil. HNO_3 forming $Sn(NO_3)_2$ and NH_4NO_3, whereas Sn is converted to SnO_2 in hot conc. HNO_3 :

$$4Sn + 10HNO_3 = 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

$$Sn + 4HNO_3 = H_2SnO_3 + 4NO_2 + H_2.$$

$$\downarrow$$

$$SnO_2 + H_2O$$

Alkali dissolves tin giving alkali metal stannate :

$$Sn + 2NaOH + H_2O = Na_2SnO_3 + 2H_2$$

Halogens directly combine with Sn to give SnX_4. Thus,

$$Sn + 2Cl_2 = SnCl_4$$

Uses of tin : (i) Tin is used in the production of tin plates which are actually iron plates coated with tin. This is widely used for making tin cans and other household utensils. The older method of tinning iron plates is to clean the surface with H_2SO_4 and then running the sheet through molten tin, known as the *hot dip* method. Now-a-days the tinning is done electrolytically.

(ii) Tin is used to make stills for distilled water.

(iii) Tin foils are used for wrapping food, but now it has been replaced by Al-foils or cellophane.

Alloys of tin : (i) Solder : Sn —50%, Pb—50% are used for soldering purpose.

(ii) Bronze : Copper and tin alloy.

(iii) Type metal : Pb—60%, Sb—30%, Sn—10%.

(iv) White metal : Sn—82 %, Sb—12%, Cu—6%.

Some Compounds of Tin

Stannous oxide, SnO : This is obtained by special method :

(a) When $SnCl_2$ is treated with Na_2CO_3 in the hot condition;

(b) heating tin oxalate in the absence of air :

$$SnCl_2 + Na_2CO_3 = SnO + CO_2 + 2NaCl$$

$$SnC_2O_4 = SnO + CO_2 + CO$$

Sn, on strong heating in air, gives SnO_2 which is yellow when hot, white when cold and is used in making opaque glass and enamels.

Stannous hydroxide, $Sn(OH)_2$: It is produced in the form of white gelatinous precipitate when Sn^{+2} compounds in solution are treated with alkali solutions :

$$SnCl_2 + 2NaOH = Sn(OH)_2 + 2NaCl$$

$Sn(OH)_2$ is dissolved in excess of NaOH to give stannite and on boiling precipitates SnO :

$$Sn(OH)_2 + NaOH = NaSn(OH)_3$$

Sodium stannite solution has great reducing properties and is used to test for Bi^{+3} when $Bi(OH)_3$ is reduced to black metallic Bi :

$$2\,Bi(OH)_3 + 3\,NaSn(OH)_3 + 3\,NaOH = 2Bi + 3Na_2Sn(OH)_6$$

Stannic acids and stannates : On adding alkali to a solution of Sn^{+4} such as $SnCl_4$, a white gelatinous mass is produced. It may be expected to have a composition of $Sn(OH)_4$, but neither the acid nor salts derived from it have been made. These have indefinite compositions and may have polymer structure.

Ortho stannic acid is formulated as $H_2[Sn(OH)_6]$ and gives the Na-salt, $Na_2[Sn(OH)_6]$. The ortho acid readily loses H_2O forming meta stannic acid or a α-stannic acid, $SnO(OH)_2$ or H_2SnO_3. This is formed when NH_4OH is added to $SnCl_4$:

$$SnCl_4 + 4NH_4OH = Sn(OH)_4 + NH_4Cl$$

$$\downarrow -H_2O$$

$$SnO_2 \xleftarrow{-H_2O} SnO(OH)_2$$

α - or meta stannic acid forms salts with alkali, giving Na_2SnO_3 which are soluble in acids.

β - stannic acid is obtained when Sn reacts with conc. HNO_3 in the hot condition and is said to have the probable composition $H_2Sn_5O_{11}.4H_2O$ because the sodium salt has been formulated as $Na_2Sn_5O_{11}.4H_2O$. Sodium stannate or meta stannate is Na_2SnO_3 and is made by fusing SnO_2 in NaOH :

$$SnO_2 + 2NaOH = Na_2SnO_3 + H_2O$$

Sodium stannate is used in calico printing.

Tin halides, SnX_4 and SnX_2 :

SnF_2 : $Sn(OH)_2 + 2HF = SnF_2 + 2H_2O$

SnF_4 : $SnCl_4 + 4HF = SnF_4 + 4HCl$

SnF_2 is a white crystalline substance whereas SnF_4 is a hygroscopic solid. It forms double compounds with NH_3. On adding HF to K_2SnO_3, potassium fluoro-stannate, K_2SnF_6 is obtained.

$SnCl_2$: It is obtained commercially as $SnCl_2.2H_2O$ by the reaction of Sn or SnO_2 with HCl. Anhydrous $SnCl_2$ is obtained by the action of HCl gas on heated Sn or by heating Sn and $HgCl_2$ together:

$$Sn + 2HCl\ (g) \rightarrow SnCl_2 + H_2$$

$$Sn + HgCl_2 = SnCl_2 + Hg$$

$SnCl_2$ is soluble in water, ether, alcohol. $SnCl_2$ is hydrolysed in water on standing forming basic Sn(OH)Cl :

$$SnCl_2 + H_2O = Sn(OH)Cl + HCl$$

$SnCl_2$ is a reducing agent because it is easily oxidized to Sn^{+4} state. A few reducing reactions of analytical use are :

(a) $2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$

$$\downarrow +SnCl_2$$

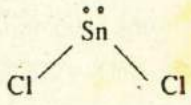
$$2Hg + SnCl_4$$

(b) $FeCl_3 + SnCl_2 \rightarrow SnCl_4 + FeCl_2$

(c) $SnCl_2 + I_2 + 2HCl = SnCl_4 + 2HI$

$SnCl_2.2H_2O$ is used in industry also as mordant in dyeing, weighting of silk, and tin-coated metal articles, such as pins and paper clips.

The structure of $SnCl_2$ is represented as,



$SnCl_4$ *:* It is obtained by the following reactions :-

(a) $Sn + \text{excess } Cl_2 \rightarrow SnCl_4$

(b) $Sn + \text{excess } HgCl_2 \xrightarrow{\text{distilled}} SnCl_4 + 2Hg$

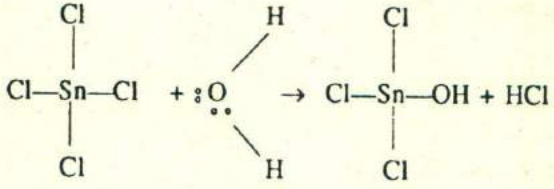
$SnCl_4$ is a colourless fuming liquid, soluble in organic solvents as in CCl_4 and non-conductor of electricity. Thus, it is a typical covalent compound. $SnBr_2$ and $SnBr_4$ are obtained in analogous manner. But when Sn and I_2 are heated together SnI_4 is formed with evolution of much heat and light. SnI_4 are red crystals soluble in organic solvents.

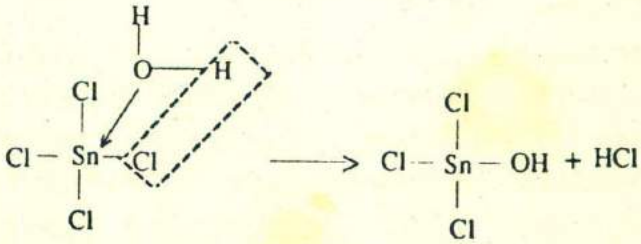
SnX_4 have tetrahedral structure.

It is to be noted that except carbon compounds, e.g., CCl_4, the tetrahalides of group IV elements are hydrolysed in water :

$$MX_4 + 2H_2O = MO_2 + 4HX$$

Thus, in covalent $SnCl_4$, since Sn is less electronegative than Cl, it carries a partial positive charge which attracts the OH ions of H_2O. Similar reaction occurs with $SiCl_4$:





The process continues untill all Cl is replaced by OH and releasing HCl. This happens in the case of $SiCl_4$ also for the same reason and the final product is $Si(OH)_4$.

Tin sulphide, SnS : When H_2S is passed into a solution of $SnCl_2$, yellow precipitate of SnS is formed. SnS is not soluble in alkali sulphides but soluble in yellow ammonium sulphide (containing large amount of S) forming thiostannate :

$$SnS + (NH_4)_2S = SnS_2 + 2NH_4^+$$

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$$

Stannic sulphide, SnS_2 : This is also known as *Mosaic Gold* and is used as a pigment in gilding. This is made by the action of H_2S on Sn^{+4}-salts :

$$SnCl_4 + 2H_2S = SnS_2 + 4HCl$$

It is also obtained by heating a mixture of Sn, NH_4Cl and S together :

$$Sn + 4NH_4Cl = (NH_4)_2SnCl_4 + H_2 + 2NH_3$$

$$2(NH_2)_2SnCl_4 + 2S = SnS_2 + 2NH_4Cl + (NH_4)_2SnCl_6$$

This is an old method, and mosaic gold is used for imparting the look of gold on such articles as made of wood.

LEAD

In lead also we come across the outermost s^2p^2 electrons after d^{10} and Pb^{+2} is more stable than Pb^{+4}.

Sources of lead :

Galena—PbS
Anglesite—$PbSO_4$
Lanarkite—$PbO.PbSO_4$
Cerussite—$PbCO_3$

The most important mineral source of Pb is galena, PbS, and it is sometimes mixed with other sulphides, such as those of Cu, Zn, Sb and Ag.

Metallurgy : PbS is easily converted to PbO by heat and PbO is easily changed to Pb by reduction with carbon or scrap iron or simply by air.

1. Air Reduction Process : The concentrated ore is roasted in reverberatory furnace under controlled supply of air. Some of the PbS is converted to $PbSO_4$ and PbO which now react with the excess of PbS and thereby reduced to metallic Pb. The molten lead is drawn off and further purified :

$$2PbS + 3O_2 = 2PbO + 2SO_2$$
$$PbS + 2O_2 = PbSO_4$$
$$2PbO + PbS = 3Pb + SO_2$$
$$PbSO_4 + PbS = 2Pb + 2SO_2$$

2. Carbon Reduction Process : The crushed and concentrated galena is converted to PbO by roasting with a slow blast of air. For this purpose PbS is mixed with lime, CaO, in order to prevent the oxidation of PbS to $PbSO_4$ and $PbSiO_4$. Even if $PbSiO_3$ is formed, it reacts with CaO to give PbO :

$$PbSiO_3 + CaO = CaSiO_3 + PbO$$

The sintered ore is then charged in blast furnace with coke and lime. PbO is thus converted to Pb. The molten lead sinks at the bottom of the furnace and the slag floats on the top of the molten lead and is drawn off from different outlets :

$$PbO + C = Pb + CO$$

$$PbO + CO = Pb + CO_2$$

The lead obtained by the above methods contains Cu, Sb, As, Bi, Au, Ag etc. as impurities. The purification of lead is done by various processes.

(a) Softening of Pb : The crude lead is melted in a shallow reverberatory furnace and stirred with a current of air. The oxides of Sb, Bi, As are formed and rise to the surface and the molten lead is drained off for further refining.

(b): Desilverisation of lead : Gold and silver are extracted from lead by : (i) *Parke's process or* (ii) *Pattinson's process.*

(i) Parke's process is based on the extraction of silver from Pb by means of Zn. In the molten state Ag goes with the Zn layer and Pb is desilverised to a great extent.

(ii) Pattinson's process is based on the fact that Pb-Ag alloy (containing 2% Ag) has lower melting point than Pb. The portion of lead which solidifies first is rich in silver.

(c) Betts' electrolytic process for pure lead : This method gives relatively purer variety of Pb and the desilverized lead is subjected to this method. Thin sheets of pure lead are the cathodes and plates of impure lead are made the anodes. The electrolyte is a solution containing lead hexafluorosilicate, $PbSiF_6$ and 10% hexafluorosilicic acid, H_2SiF_6. The pure lead deposits on the cathodes which grow in bulk.

Uses of lead : The uses of lead depend mainly on the ease with which it is worked, its low melting point and resistance to corrosion. Some of the uses of lead are :

(1) Plumbing articles, but now replaced by galvanized iron materials.

(2) Manufacture for lead accumulators.

(3) Covering for electric cables.

(4) Lead chambers in H_2SO_4 plants.

(5) Making lead shots and bullets.

(6) Manufacture of white lead and other pigments.

(7) Making alloys, such as solder, type metal, pewter etc.

Alloys : (1) Type metal : Pb—82%, Sb—15% and Sn—3%.

(2) Solder : Pb—50%, Sn—50%.

(3) Pewter : Pb—20%, Sn—80%.

Compounds of Lead

The common oxidation state of Pb is +2. The +4 oxidation state is seldom formed because the two s^2 electrons in Pb remain associated with the core as a stable electron pair. Because of the high oxidation potential of Pb^{+4}, i. e., $Pb^{+2} \rightarrow PbO_2$, –1.5 volts, Pb^{+2} is the characteristic oxidation state.

Oxides of lead, PbO, Pb_3O_4 and PbO_2 : PbO is known as *litharge*. This is obtained by heating Pb or PbS in air, in the form of yellow-orange powder. This oxide is soluble in acids and alkalies forming Pb^{+2} or $HPbO_2^-$ ions respectively. It is used in the manufacture of lead glass and enamels. A mixture of PbO and glycerine is used as a cement since it sets to a solid lead glyceride. PbO is used in making NaOH also :

$$5PbO + 2NaCl + H_2O \rightleftharpoons PbCl_2.4PbO + 2NaOH$$

Red lead : Pb_3O_4 or *red lead* is made by careful heating of PbO in air at temperatures between 400—500°C. It is decomposed to PbO on strong heating :

$$6PbO + O_2 \rightleftharpoons 2Pb_3O_4$$

When Pb_3O_4 is treated with HNO_3, 2/3 of it dissolves as $Pb(NO_3)_2$ and 1/3 remains as PbO_2 :

$$Pb_3O_4 + 4HNO_3 = PbO_2 + Pb(NO_3)_2 + 2H_2O$$

For this reason, Pb_3O_4 is considered as a plumbate of Pb having 2PbO. PbO_2 or $PbPb_2O_4$ composition having Pb^{+2} as cation and Pb^{+4} in the anion PbO_4^{-4}.

Pb_3O_4 (red lead) is used as paints, making storage batteries, ceramic products and lint glass. Paint of red lead acts as a rust inhibitor for iron and woodwork.

Pb_2O_3, which is a yellow solid, is also formulated as $Pb(PbO_3)$. This is also made from PbO when heated in air.

PbO_2, lead dioxide or lead peroxide is obtained as a dark chocolate-brown powder by various methods. These methods are :

(1) $Pb_3O_4 + 4HNO_3$ (conc.) = $PbO_2 + 2Pb(NO_3)_2 + 2H_2O$.

(2) Oxidation of PbO with alkaline Cl_2 :

$$PbO + NaClO = PbO_2 + NaCl$$

(3) Anodic oxidation of solutions of Pb^{+2} salts :

$$Pb^{+2} + 2H_2O = PbO_2 + 4H^+ + 2e$$

(4) Fusion of PbO with $KClO_3$ and KNO_3.

(5) Action of bleaching powder on lead acetate gives PbO_2 :

$$Pb(CH_3COO)_2 + Ca(OH)_2 = Pb(OH)_2 + (CH_2COO)_2Ca$$

$$Pb(OH)_2 + CaOCl_2 = PbO_2 + CaCl_2 + H_2O$$

PbO_2 is a powerful oxidizing agent since Pb^{+4} tends to revert to stable +2 state by gaining 2 electrons. PbO_2 readily loses oxygen and is converted to PbO on heating or even in light. With concentrated HCl it liberates Cl_2, but with cold HCl it gives solution of $PbCl_4$:

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$$

$$PbO_2 + 4HCl = PbCl_4 + 2H_2O$$

It dissolves in concentrated alkalies to form lumbates. PbO_2 is the principal constituent of the anode of the charged lead storage batteries.

The structure or PbO_2 is, O = Pb = O

Lead halides, PbX_2 and PbX_4 : $PbCl_2$ is formed from Pb and Cl_2 or by dissolving PbO in HCl or by adding Cl^- ion to a solution of Pb^{+2} salts. PbF_2 is prepared in the same manner :

$$Pb(NO_3)_2 + 2NaCl = PbCl_2 + 2NaNO_3$$

$PbCl_2$ is soluble in hot water but reappears on cooling.

H_2PbCl_4 is formed when $PbCl_2$ is treated with conc. HCl.

$PbCl_4$ is not a stable compound and is formed when PbO_2 reacts with cold HCl.

$PbBr_2$ and PbI_2 are obtained by double decomposition of a soluble Pb^{+2} salt and soluble KBr or KI respectively. PbI_2 forms beautiful golden spangles soluble in hot but insoluble in the cold condition.

Lead sulphate, $PbSO_4$: It is formed as an insoluble white precipitate on adding a soluble sulphate or dil. H_2SO_4 to a lead salt solution :

$$Pb(NO_3)_2 + Na_2SO_4 + PbSO_4 + 2NaNO_3$$

$PbSO_4$ is soluble in ammonium acetate or alkali solutions :

$$PbSO_4 + 2NH_4COOCH_3 \rightleftharpoons Pb(CH_3COO)_2 + (NH_4)_2SO_4$$

With hot conc H_2SO_4 it gives a solution of $H_2Pb(SO_4)_2$ from which $PbSO_4$ is precipitated out on dilution.

Lead nitrate, $Pb(NO_3)_2$: It is formed when Pb or PbO is dissolved in HNO_3. It is soluble in water to give a stable solution only in presence of a little HNO_3, otherwise hydrolysed to give $Pb(OH)NO_3$:

$$Pb(NO_3)_2 + H_2O \rightleftharpoons Pb(OH)NO_3 + HNO_3$$

$Pb(NO_3)_2$ is decomposed on heating as other nitrates of heavy metals :

$$Pb(NO_3)_2 \rightarrow 2PbO + 4NO + 3O_2$$

Lead acetate, $Pb(OOCCH_3)_2$: It is one of the few soluble salts of lead and was known as sugar of lead since it has sweet taste. It is obtained by dissolving $PbCO_3$ or PbO in acetic acid. In presence of excess PbO, basic lead acetate is obtained:

$$PbO + 2CH_3COOH \rightarrow Pb(OOCCH_3)_2 + H_2O$$

Lead chromate, $PbCrO_4$: It is insoluble in water and is obtained by double decomposition reactions :

$$2Pb(CH_3COO)_2 + K_2Cr_2O_7 \rightarrow 2PbCrO_4 + 2KCH_3COO + CH_3COOH$$

$$Pb(NO_3)_2 + K_2CrO_4 = PbCrO_4 + 2KNO_3$$

It is known as "chrome yellow" and is used as a pigment. When the yellow $PbCrO_4$ is boiled with alkali, a basic Pb chromate, $Pb(OH)_2.PbCrO_4$, is obtained which is orange coloured and is used as a pigment.

$$2PbCrO_4 + 2NaOH = Pb(OH)_2.PbCrO_4 + Na_2CrO_4$$

Lead tetraethyl, $Pb(C_2H_5)_4$: It is a covalent compound and liquid at ordinary temperatures. It is used as petrol additive for producing "antinock" gasoline. It is obtained by the reaction of ethyl chloride with a Na—Pb alloy :

$$4C_2H_5Cl + Na_4Pb = Pb(C_2H_5)_4 + 4NaCl$$

Lead carbonate, $PbCO_3$: The normal carbonate is obtained by the action of $NaHCO_3$ upon $PbCl_2$ or $PbSO_4$:

$$PbCl_2 + NaHCO_3 = PbCO_3 + NaCl + HCl$$

"White lead" or the basic lead carbonate : The basic Pb carbonate has the composition $Pb(OH)_2.2PbCO_3$. This is formed when alkali carbonates are added to solutions of Pb-salts. Until a few years ago the manufacture of white lead was an important chemical industry because of its commercial importance as the paint pigment. It has a good covering power but with time the white paint turns black because of its conversion to PbS due to the action of H_2S which may be present in some places like industrial areas. The large scale development of the titanium dioxide, TiO_2, as a white pigment has almost completely replaced "white lead" industry because TiO_2 is free from the darkening effects. However, a short description of the manufacture of white lead is of interest from the point of view of chemistry.

White lead is manufactured by the action of air, CO_2 and CH_3COOH vapour on metallic Pb. Various technical procedures are adopted to bring about the reactions such as the Dutch Chamber Process in which the bars of Pb are exposed to the action of CH_3COOH vapour and CO_2 in a suitable chamber. In the Carter Process the corrosion of Pb is carried out in wooden cylinders where molten lead is atomised with superheated steam and a spray of CH_3COOH and a stream of CO_2 are introduced. The essential reactions are :

$$2Pb + O_2 + 2CH_2COOH = 2Pb(OH)COOCH_3$$

$$6Pb(OH)COOCH_3 + 2CO_2 = Pb(OH)_2.2PbCO_3 + 3Pb(COOCH_3)_2 + 2H_2O$$

$Pb(COOCH_3)_2$ is used up in the process and CH_3COOH is regenerated which again reacts with more lead. The process is continuous and white lead is removed from the stacks.

Titanium, Zirconium and Hafnium: These group IVB elements are classed as transition metals. Outermost electron groups are :

$$Ti—3d^24s^2 \qquad Zr—4d^25s^2 \qquad Hf—5d^26s^2$$

They are ordinarily tetravalent (+4 state), but also show oxidation states of +2 and +3. These metals are difficult to isolate. Titanium is found as *rutile*, TiO_2, and *ilmenite*, $FeTiO_3$.

Ti is very difficult to obtain in the pure form because of its high melting point (1800°C).

In order to get titanium, its ore is first converted into $TiCl_4$ by the reaction :

$$2TiO_2 + 3C + 4Cl_2 \xrightarrow{700°—1000°C} 2TiCl_4 + 2CO + CO_2$$

$TiCl_4$ is first purified and then metallic titanium is obtained by the reaction with active metals, such as Na, K, Ca, Mg etc. (Kroll process).

$$TiCl_4 + 2Mg \longrightarrow Ti \text{ (spongy)} + 2MgCl_2$$

The spongy titanium is converted to metallic titanium by treatment with dilute sulphuric acid or by the reaction with iodine to form TiI_4 which is decomposed by heating to 800°C in vacuum depositing pure titanium (Van Arkel Process). Iodine in the vapour state is used over and over again :

$$TiI_4 \longrightarrow Ti + 2I_2$$

Uses of Ti : Special properties of Ti has been used to make special alloys, such as in jet motors and high speed aircraft. Ferrotitanium has been used in special steels of great strength. TiO_2 is largely used as pigment in paint industry and is made from ilmenite, $FeTiO_3$, by reaction with HCl and subliming $FeCl_3$:

$$2FeTiO_3 + 4HCl + Cl_2 = 2FeCl_3 + 2TiO_2 + 2H_2O$$

$TiCl_4$ is liquid and is made by passing Cl_2 gas on TiO_2 mixed with C in the heated condition :

$$TiO_2 + C + 2Cl_2 = TiCl_4 + CO_2$$

$TiCl_4$ is used to produce smoke screen. $TiCl_2$ and $TiCl_3$ are good reducing agents.

Zirconium and hafnium occur together in nature. The chief ore is *zircon*, $ZrSiO_4$. All minerals of Zr contain about 5% Hf. The chemical properties of Zr and Hf are almost similar due to the effect of lanthanide contraction giving almost same ionic sizes of both.

ZrO_2 is also known as "Zirconia' and HfO_2 as 'Hafnia'. They are refractory materials and have very high melting points. The metals are obtained by heating K_2ZrF_6 or K_2HfF_6 with metals, such as Na, K or Al.

$ZrCl_4$ is hydrolysed to the extent of $ZrOCl_2$ whereas $TiCl_4$ is hydrolysed to the hydrated oxide TiO_2.

QUESTIONS AND PROBLEMS

1. Describe how coal gas is manufactured. What are its main constituents and how does it differ from producer gas and water gas? Give reasons why hydrogen sulphide is always removed from coal gas and explain the chemical reactions involved in its removal.
2. Describe preparation, properties and uses of lead chromate and basic lead chromate.
3. Write short notes on the preparation and uses of the following fuel gases :—
   (a) Producer gas, (b) Water gas and semi-water gas, (c) Coal gas.
4. Describe the preparation, properties and uses of —
   (a) Calcium cyanamide.
   (b) Calcium carbide.
   (c) Water glass.
   (d) Water gas.
5. Describe the preparation, properties and uses of—(a) Sodium cyanide, (b) Water gas, (c) Carbon disulphide.
6. Describe the preparation and uses of :— (a) Water gas, (b) White lead.

7. How would you prepare lead chromate from lead monoxide and chromium oxide?
8. Compare the chemistry of carbon and silicon and some of their important compounds. Mention salient points only.
9. How tin is extracted from tinstone and how the metal is purified? Discuss the action of :—(a) HCl, (b) HNO_3 and (c) NaOH on tin.
10. Write brief description of the preparation and uses of :— (a) Water gas, (b) Producer gas.
11. How are carborundum and water glass prepared ?
12. Describe the preparation, properties and uses of lead.
13. Compare the nature of the bonds in $PbCl_2$ and $PbCl_4$.
14. Show by suitable equations that $Pb(OH)_2$ is amphoteric.
15. Discuss the properties of group IVA elements in relation to their electronic structures. Explain why tin and lead do not form stable +4 oxidation states.
16. Explain :—
    (a) The inert pair of electrons.
    (b) Hydrolysis of silicon and tin tetrachlorides.
    (c) Tin disease.
    (d) Desilverisation of lead.
17. Discuss the principles involved in the extraction of lead from galena by air roasting process and the reduction process.
18. Compare the chemistry of group IV elements with particular reference to C, Si, Ge, Sn and Pb.
19. What is the theoretical basis of charcoal reduction test in the qualitative chemical analysis?
20. 'Properties of boron and silicon are similar in many respects. Discuss.
21. In Periodic group IVA carbon is a nonmetal, silicon and germanium are metalloids, tin and lead are metals. Explain why this is so.
22. Can you design construction of coinage and fuselage of pure tin? If not, why?
23. Zinc and tin are both used as protective coating for steel. What is the mechanism by which protection occurs in each case.
24. What are the structural formulae of stannic acid and stannous acid?
25. Write the equation showing production of hydrogen by the action of strong alkali solution on tin.
26. Describe Parke's process for the desilverization of lead. For what specific reasons Betts' process is employed.

27. Could you suggest replacing the lead plates in a storage battery by other metals ?
28. What are the uses of titanium metal and TiO_2 ?
29. Point out the commercial use of $TiCl_4$.
30. Zirconium and hafnium have very close resemblance of chemical properties. Discuss.

CHAPTER 20

NITROGEN AND PHOSPHORUS

(The elements of Group V)

The elements of group V are sub-divided into group VA and VB as follows:—

Group VA	*Group VB*
N — Nitrogen	
P — Phosphorus	V — Vanadium
As — Arsenic	Nb — Niobium
Sb — Antimony	Ta — Tantalum
Bi — Bismuth	

In group VA non-metallic character is more pronounced as compared to those of group IVA. The metallic character increases at the bottom of group VA, particularly Sb and Bi are considered to be metallic elements.

The electronic structures of group VA elements are given in Table 20.1.

Table 20.1. Electronic structures of group VA elements.

At. No.	*Elements*	*Electronic structures*	*Valence electrons*
7	N	He core, $2s^2 2p^3$	$2s^2 2p^3$
15	P	Ne core, $3s^2 3p^3$	$3s^2 3p^3$
33	As	Ar core, $3d^{10} 4s^2 4p^3$	$4s^2 4p^3$
51	Sb	Kr core, $4d^{10} 5s^2 5p^3$	$5s^2 5p^3$
83	Bi	Xe core, $4f^{14} 5d^{10} 6s^2 6p^3$	$6s^2 6p^3$

Thus the 5 electrons in the outermost energy levels are s^2p^3 electrons in each case. The group VB elements V, Nb, and Ta are transition metals and have

the electronic configurations in which **d** electron levels have the following configurations :—

V (23) — Ar core, ... $3d^3 4s^2$

Nb(41) — Kr core, ... $4d^4 5s^1$

Ta (73) — Xe core, ... $5d^3 6s^2$

Physical Properties

The physical properties of the group VA elements, N, P, As, Sb and Bi and also VB elements, are given in Table 20.2 (a) and (b) respectively.

Table 20.2 (a). Physical properties of group VA elements.

Properties	*N*	*P*	*As*	*Sb*	*Bi*
Atomic No.	7	15	33	51	83
Atomic Wt.	14.01	30.98	74.91	121.76	209.00
Outer electron configuration	$2s^2 2p^3$	$3s^2 3p^3$	$4s^2 4p^3$	$5s^2 5p^3$	$6s^2 6p^3$
Covalent radius (Å)	0.74	1.10	1.25	1.44	1.45
Ionic radius M^{+5}	0.11	0.34	0.47	0.62	0.74
Ionization energy (ev)	14.50	11.00	10.00	8.60	8.00
Melting point (°C)	−210	44 (white)	817	630 (sublimes)	271
Boiling point (°C)	−196	280	633	1640	1560
Electronegativity	3.07	2.10	2.00	1.80	1.70
Oxidation states	−3 to +5	−3. 0. 1,3,4,5,	0, 3, 5,	0, 3, 5	0, 3, 5
Oxidation potential (v)	N^{+3}/N^{+5}	P^{+3}/P^{+5}	As/As^{+3}	Sb/Sb^{+3}	Bi/Bi^{+3}
	−0.94	+0.49	−0.25	−0.21	−0.32

Thus we see from the Table 20.2 (a) that transition from non-metallic properties is very much pronounced. N and P are primarily non-metals whereas Sb and Bi show metallic behaviour. Arsenic exists in several forms and sublimes before it boils. N_2 molecule is one of the most stable molecules and requires more than 225 kcal to break into atoms. P is less stable.

As mentioned before V, Nb and Ta are transition elements and have metallic properties of heavy elements [Table 20.2 (b)].

Table 20.2 (b). Physical properties of group VB elements.

Properties	*V*	*Nb*	*Ta*
Atomic No.	23	41	73
Atomic Wt.	50.95	92.91	180.88
Outer electron configuration	$3d^3 4s^2$	$4d^4 5s^1$	$5d^3\ 6s^2$
Covalent radius (Å)	1.31	1.41	1.43
Ionic radius M^{+5}	0.59	0.70	0.71
Ionization energy (ev)	6.70	6.50	6.10
Melting point (°C)	1710	2450	2850
Boiling point (°C)	3000	3300	4100
Electronegativity	1.45	1.23	1.33
Oxidation states	+2, +3	+3, +4	+3, +4
	+4, +5	+5	+5
Oxidation Potential (v)	V/V^{+2}	Nb/Nb^{+5}	Ta/Ta^{+5}
	1.5	0.62	0.71

Chemical Properties of N, P, As, Sb and Bi

The outermost electronic configurations of N, P, As, Sb and Bi all have s^2p^3 electrons making the total number of valence electrons equal to 5. The oxidation states of these elements show that N forms compounds having oxidation states −3, −2, −1, 0, +1, +2, +3, +4 and +5. Phosphorus has oxidation states −3, 0, +1, +3, +4, +5. But As, Sb, Bi are known to give oxidation states of 0, +3 and +5 only. In +3 compounds the two unshared electrons are s electrons or as hybrid of s and p orbitals.

The electronegativity values from N to Bi indicate that the elements tend to form covalent compounds with non-metals. In the covalent compounds of N, a total number of electrons around the N nucleus is never greater than 8 since only s and p orbitals are available for sharing of electrons. Thus the electron structure of N atom may be represented by :

$$1s^2 2s^2\ 2p_x^1 2p_y^1\ 2p_z^1$$

using three bonds. The other elements of this group may form bonds by utilising their d orbitals. Thus N forms NH_3 and NCl_3, but P in addition to PH_3 and PCl_3, can also form PCl_5 and PF_5. In aqueous solutions, P, As, Sb tend to form 4 bonds rather than 3 even in their trivalent derivatives.

Thus in chemical properties, these five elements show regular gradation of properties which are characteristics of group relationships. Some of the points of similarities and gradations in properties may be cited as follows :—

(1) N being most electronegative, forms more stable nitrides with metals having probably ionic bond. Phosphides and arsenides are formed but are not very stable. No such compounds are formed by Sb and Bi which give alloys.

(2) The stability of the hydrides, MH_3, decreases markedly, NH_3 is a stable compound, PH_3 unstable and AsH_3 very unstable. SbH_3 and BiH_3 have fleeting existence. The basic properties also decrease from NH_3 to PH_3 to AsH_3. NH_3 is most basic but PH_3 is less so, whereas AsH_3 does not combine with acids at all.

(3) Numerous oxides are formed by N and P and others but the acidic character decreases from N to Bi. Thus,

N_2O_3		
P_2O_3		
N_2O_5	As_2O_3	Bi_2O_3
P_2O_5	Sb_2O_3	
Distinctly acidic	Amphoteric	Distinctly basic

As_2O_5 and Sb_2O_5 are unstable. Bi_2O_5 has not been isolated, but sodium bismuthate, $NaBiO_3$, having Bi^{+5} is a well-known oxidizing agent.

(4) N and P and all the others of this group give trichlorides and oxychlorides. But they are hydrolysed in different manners indicating the change from non-metallic state. Thus,

$$NCl_3 + 3H_2O = NH_3 + 3HOCl$$
$$PCl_3 + 3H_2O = 3HCl + H_3PO_3$$
$$AsCl_3 + H_2O = \text{Not hydrolysed}$$
$$SbCl_3 + H_2O = SbOCl + 2HCl$$
$$BiCl_3 + H_2O = BiOCl + 2HCl$$

Sb and Bi may have normal salts in concentrated solution of the acids, such as $BiCl_3$ in conc HCl or $Sb_2(SO_4)_3$ in conc H_2SO_4. But in water they form oxy-salts which come out as precipitates. BiF_3 and BiI_3 are insoluble in cold water and are inert.

(5) Normal compounds containing SO_4^{-2}, NO_3^{-1}, CO_3^{-2} are not formed by N, P, As and even by Sb. Such salts of Bi are known.

The behaviour of the gradation of properties from N to Bi indicates that the transition from non-metal to metal takes place gradually. N and P are definitely non-metal. As and Sb may be classed as metalloidic while Bi is distinctly metallic in character. It is to be noted that +3 state of N. P and As exists as oxyacids in aqueous media. The more basic Sb^{+3} and Bi^{+3} exist as positive ions giving BiOCl and SbOCl. The metallic character of Bi may be attributed to the greater distance of the valence electrons from the nucleus which has much less attraction for p^3 electrons in bismuth making the $6s^2$ electrons quite inert. The chemistry of nitrogen and phosphorus are now described separately. After one has grasped the family behaviour as outlined above, the descriptive chemistry of the elements will be easier to remember.

NITROGEN

Nitrogen is one of the most useful elements. Along with phosphorus it is an essential element for plant and animal life.

Sources of nitrogen : (1) Air—78% by volume.

(2) Chile salpetre, $NaNO_3$, and salt petre, KNO_3.

(3) Soil contains NH_4-salts and nitrates.

(4) Animal and vegetable materials as in proteins and plants.

Preparation of nitrogen : (1) Nitrogen is most conveniently isolated from the air in which it is present to the extent of about 78% by volume. Various methods have been adopted to separate nitrogen from air. For example.

(a) When air is passed through KOH to absorb CO_2 and H_2O and and then through heated copper for removing oxygen as CuO, nitrogen is obtained. In a small scale oxygen may be removed by burning phosphorus.

(b) On industrial scale nitrogen is obtained by fractional distillation of liquid air.

Nitrogen isolated from air by either method may contain small quantities of oxygen and inert gases of which argon is the main constituent.

(2) Pure nitrogen is obtained by heating a solution of ammonium nitrite, NH_4NO_2, which decomposes to give N_2 :

$$NH_4NO_2 = N_2 + 2H_2O$$

In practice, a mixture of $NaNO_2$ with NH_4Cl is heated gently to start the reaction. NH_4NO_2 is normally difficult to store because it is unstable :

$$NH_4Cl + NaNO_2 = NaCl + 2H_2O + N_2$$

(3) Nitrogen is also obtained by the oxidation of NH_3. Various methods have been adopted for the reaction :—

(a) NH_3 passed over heated CuO gives N_2 :

$$2NH_3 + 3CuO = 3H_2O + N_2 + 3Cu$$

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

(c) $2NH_3 + 3CaOCl_2 = 3CaCl_2 + 3H_2O + N_2$

(4) Ammonium dichromate, $(NH_4)_2Cr_2O_7$, when heated, N_2 is evolved vigorously (volcano experiment) :

$$(NH_4)_2Cr_2)_7 = Cr_2O_3 + 4H_2O + N_2$$

(5) When sodium azide, NaN_3, is heated very pure nitrogen is obtained :

$$2NaN_3 = 2Na + 3N_2$$

(6) Urea on heating with a nitrite in presence of H_2SO_4 gives N_2 :

$$NH_2CONH_2 + 2HNO_2 = CO_2 + 3H_2O + 2N_2$$

Properties of nitrogen : Nitrogen exists as a diatomic gas, N_2 at ordinary temperature. The gas is colourless and only slightly soluble in water. It does not support combustion or respiration but it is not poisonous. The lack of reactivity in nitrogen molecule, N_2, may be attributed to the triple bond which is the most stable diatomic molecule :

$$:N:::N: \quad \text{or} \quad N \equiv N$$

N_2 colecule contains one σ bond and two π bonds between N atoms and thereby rotation between N atoms is impossible. In order to dissociate N_2

molecule into atoms, 225 Kcals/mole are required. Thus the lack of chemical reactivity of N_2 and easy decomposition of many nitrogen compounds to give N_2 can be explained.

The triple bond is nitrogen is different from other triple bonds and does not show tendency to undergo addition reactions. for instance, acetylene, HC ≡ CH, organic nitriles, RC ≡ N, and some nitroso compounds, (N ≡ O⁺), have triple bonds but show great reactivity and undergo addition and displacement reactions. N_2 reacts only at high temperature by fist becoming active due to elevation of bonding electrons to higher energy levels followed by triple bond breaking into N = N and then N—N and finally N in atomic condition.

Nitrogen is a very electronegative element and assumes every oxidation state from −3 to +5 as shown in the following compounds :—

Compounds	*Oxidation states*
NH_3, NH_4^+	−3
N_2H_4 (Hydrazine)	−2
NH_2OH (Hydroxylamine)	−1
N_2 (element)	0
N_2O (Nitrous oxide)	+1
NO (Nitric oxide)	+2
N_2O_3 (Nitrogen trioxide) HNO_2 (Nitrous acid)	+3
NO_2 (Nitrogen peroxide) N_2O_4 (Nitrogen tetroxide)	+4
N_2O_5 (Nitrogen pentoxide) HNO_3(Nitric acid)	+5

Reactions of Nitrogen

1. N_2 reacts with H_2 at about 600°C in presence of catalyst (Fe and Mo) and under pressure to give NH_3 (Haber process) :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 23.8 \text{ Kcals}$$

2. N_2 reacts with O_2 under the influence of electric spark. This happens also at the time of lightning flashes in the atmosphere and NO is formed which combines with more O_2 to give NO_2 :

$$N_2 + O_2 \rightleftharpoons 2\,NO_2 - 43.2 \text{ Kcals}$$

$$NO + O_2 \rightarrow NO_2 \rightarrow N_2O_4$$

3. N_2 reacts with CaC_2 at high temperatures to give $CaCN_2$:

$$CaC_2 + N_2 = CaCN_2 + C$$

4. Some metals, such as Li, Ca, Mg, Ti etc. react with N_2 at high temperature to give nitrides containing N^{-3} ions :

$$N_2 + 3Mg = Mg_3N_2$$

$$N_2 + 2Al = 2AlN$$

$$N_2 + 6Li = 2Li_3N$$

5. Al_2O_3 reacts with N_2 in presence of C at high temperature to give AlN ;

$$N_2 + Al_2O_3 + 3C = 2AlN + 3CO$$

6. N_2 reacts with a mixture of Na_2CO_3 and C on heating to give NaCN :

$$N_2 + 4C + Na_2CO_3 = 2NaCN + 3CO$$

7. N_2 does not combine with halogens by direct reactions because of high heat of formation.

Uses of Elementary Nitrogen

(1) Large quantities of N_2 are used in "fixing" atmospheric nitrogen, such as making NH_3 which in turn are used to manufacture fertilizers, nitric acid and other nitrogen compounds.

(2) Nitrogen is used to provide an inert atmosphere in certain chemical processes.

(3) High temperature mercury thermometers are filled with N_2 to measure temperature upto 500°C.

(4) For preservation of food in tin cans which are filled with N_2.

Atomic nitrogen : When a stream of nitrogen is passed under very low pressure through a tube and subjected to high tension discharge, it produces a

glow of yellow colour. This has been attributed due to the production of atomic nitrogen in the active form but there are some doubt about its atomic nature although experiments prove that it is more reactive than ordinary nitrogen.

The nitrogen cycle : Atmospheric nitrogen is the source of all nitrogen containing substances. Nitrogen is also an essential constituent of all plants and animals. Plants obtain their nitrogen through their roots mainly in the form of ammonium and nitrate compounds. Legumens, such as peas, get the nitrogen from air by means of nitrogen fixing bacteria found in the nodules on their roots. These nitrosifying and nitrifying bacteria convert atmospheric nitrogen into nitrites and nitrates which are assimilated by plants in the form of proteins. Quite a large quantity of nitrogen is converted to NO by the photochemical and electrical phenomena in the atmosphere. NO takes up more O_2 from air to become NO_2 forming HNO_2 and HNO_3 with water. These acids are washed down to the soil by rain water and react with oxides to form nitrites and nitrates in the soil. Soil bacteria also oxidize the nitrites to nitrates. Also some bacteria change ammonia into nitrites while denitrifying bacteria decompose nitrites and nitrates to free N_2 which goes to the air.

Animal get the nitrogen in the form of proteins by feeding on plants and other animals. When these animals and plants are dead, the decay products of both return nitrogen to the soil in the form of nitrates and ammonia and then the free nitrogen goes back to the atmosphere. Thus a complex cycle of N_2 from air through the soil to the plants and animals and then to the air maintains the nitrogen balance in nature.

Fixation of Atmospheric Nitrogen

Fixation of atmospheric nitrogen involves the combination of nitrogen of the air with some other elements to form subsequently useful compounds. The various processes used for the fixation of atmospheric nitrogen are :—

1. The Haber Process for NH_3 :

$$N_2 + 3H_2 \xrightarrow[200 \text{ atmos}]{600°C} NH_3$$

2. The Arc Process for NO :

$$N_2 + O_2 \xrightarrow[\text{electric arc}]{2000°C} 2NO$$

3. The Cyanamide Process for $CaCN_2$:

$$CaC_2 + N_2 \xrightarrow{1000°C} CaCN_2^-$$

4. The metallic Nitride Process forming AlN :

$$Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO$$

5. By the nitrifying bacteria in the soil nitrogen is fixed.

These processes have been described in their respective places in this book. The primary products, such as NH_3, NO, $CaCN_2$, AlN are generally converted to other useful nitrogen compounds or are used as such where possible. The processes mainly aim at the production of fertilizers.

Compounds of Nitrogen

Ammonia

This is the most important hydride of nitrogen having formula NH_3. Other hydrides of nitrogen are N_2H_4 (hydrazine) and hydrazoic acid or azoimide, HN_3.

NH_3 is present in small quantities in air due to the decay action of nitrogenous organic matters.

Preparation and production of NH_3 : In the laboratory ammonia gas is usually prepared by heating an ammonium salt with calcium hydroxide or lime. Any alkali evolves NH_3 from ammonium salts but CaO is preferred because of its cheapness and drying action :

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O$$

Metal nitrides may also be decomposed by reaction with H_2O to produce NH_3 by hydrolysis :

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$

Production of NH_3

(1) From coal : During the destructive distillation of coal, ammonia gas comes off with the coal gas along with many other volatile products. It is dissolved in water and the resulting solution when treated with lime gives off

pure ammonia which is either absorbed in water to produce liquor ammonia or else absorbed in H_2SO_4 to form $(NH_4)_2SO_4$ and is used as a fertilizer.

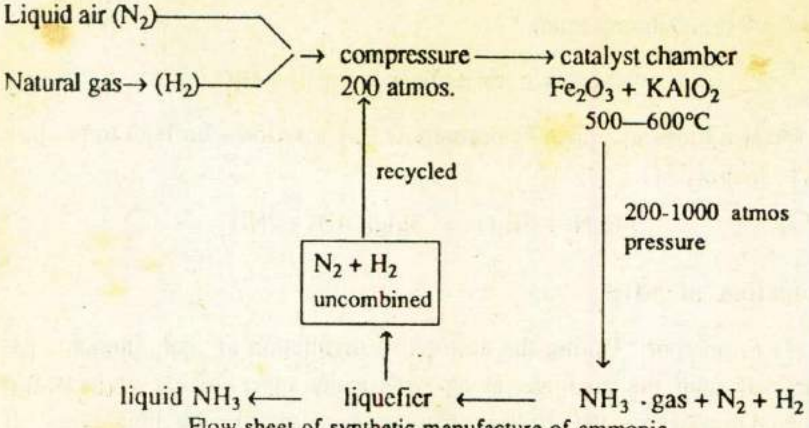
(2) *The Haber Process*"

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 23.8 \text{ Kcal}$$

The above reaction between N_2 and H_2 developed by Haber is an exothermic and reversible reaction and the equilibrium constant K is given by the expression $K = \frac{[NH_3]^2}{[N_2][H_2]^3}$ Decrease in volume and evolution of heat occur. Hence low temperature and high pressure give greater yield of ammonia. But the reactivity of N_2 with H_2 at low temperatures is so low that no NH_3 is produced. Even at high pressure the yield is very small. Haber solved the difficulties by means of using heterogeneous catalyst. Of the many catalysts, such as—(a) finely divided Fe mixed with Mo, (b) Fe_2O_3 mixed with SiO_2; (c) Ni and sodamide etc., the more efficient catalyst has been a mixture of Fe_2O_3 and potassium aluminate. Temperature of 500°C and pressure from 200 atmospheres to 1000 atmospheres have been used to get the maximum yield.

N_2 from liquid air and H_2 from water gas or natural gas are the main sources of the gases.

NH_3 is removed by liquefaction and the residual or uncombined H_2 and N_2 are recycled through the reaction chamber. The flow sheet of the process may be represented simply as :



Flow sheet of synthetic manufacture of ammonia.

(3) *The Cyanamide Process* : CaO on heating with C in an electric furnace gives CaC_2 and when N_2 is passed over crushed CaC_2 mixed with some $CaCl_2$ at 1100°C, $CaCN_2$ is formed.

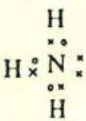
$CaCN_2$ on hydrolysis with steam under pressure in an autoclave gives NH_3:

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

NH_3 evolved is absorbed in water or is converted to other ammonium compounds, such as $(NH_4)_2SO_4$ or urea.

Physical properties : (1) It is colourless gas with characteristic irritating odour. (2) It is lighter than air. (3) It is easily liquefied. The liquid boils at −33.35°C and turns to white crystalline solid on cooling. (4) The heat of vaporisation of liquid NH_3 is very high except water, and hence used as a refrigerant. (5) NH_3 is soluble in water, ether and alcohol. NH_3 is completely removed from the aqueous solution on boiling.

Chemical properties : (1) The weakly basic character of ammonia is very familiar and most of the chemical properties of NH_3 can be explained from its structure. The Lewis structure is :



But the structure of NH_3 has been proved to be tetrahedral using sp^3 hybrid orbitals by N in NH_3 as given in Fig. 20—1 with the lone pair at one corner of the tetrahedraon.

The pair of electrons $2s^2$ have acquired bonding characteristic due to its merging with the **p** orbitals and forming sp^3 hybrid orbitals :

N— $1s^2$ $\boxed{2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1}$

sp^3

The lone pair situated at one corner of the tetrahedron occupies large volume of electron cloud and repels the N—H bonds which accounts for the large angle between H—N—H of about 107°. If NH_3 is formed by pairing of electrons in the simple $2p_x^1 2p_y^1 2p_z^1$ orbitals of N with one electron from each of the three

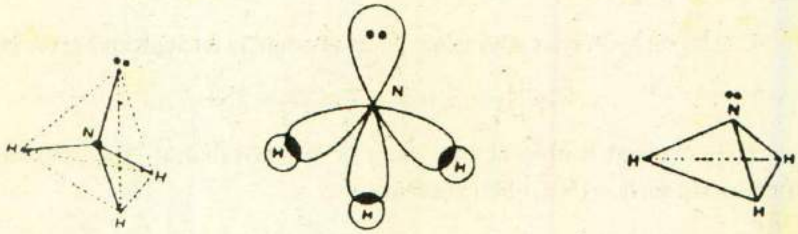


Fig. 20—1. Shape of NH_3 molecule. In effect, the shape of NH_3 will be pyramidal because of the lone pair occupying one corner of the tetrahedron. (a) Tetrahedral model, (b) Overlap of s orbitals of 3 hydrogen with sp^3 orbitals of N, (c) Effective pyramidal model.

H atoms, the angle between each H—N—H should have been 90° since p_x, p_y and p_z are at right angles to each other. Hence the bonding lone pair NH_3 is responsible for its chemical properties. Thus,

(a) $H_3N: + H^+ \longrightarrow [NH_4]^+$

(b) $H_3N: + H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H \longrightarrow H_3N:H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H$

$$\downarrow$$

$$[NH_4]^+ + [OH]^-$$

(c) $H_3N: + \underset{F}{\overset{F}{B}}:F \rightarrow H_3N:BF_3$

(d) Hydrogen bonding in NH_3 molecules and in its aqueous solution.

(2) For the same reason H_3N : forms a large number of complexes with metal ions :

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$

$$Cu^{+2} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{+2}$$

$$Cr^{+3} + 6NH_3 \rightleftharpoons [Cr(NH_3)_6]^{+3}$$

(3) NH_3 also shows weakly acidic properties since the three H may be replaced by metals :

H	H	H	Li
|	|	|	|
H—N	Na—N	Ag—N	Li—N
|	|	|	|
H	H	Ag	Li
ammonia	sodium amide	silver imide	lithium nitride

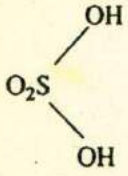
The compounds are formed when the metals are heated in NH_3 gas. But these compounds are readily hydrolysed in H_2O since H_2O is a stronger acid than NH_3 :

$$NaNH_2 + 2H_2O = NaOH + NH_4OH$$

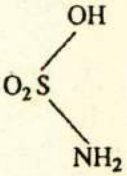
(4) Comparison of H_2O and NH_3 systems : There is analogy in the amides H—NH_2 and water H—OH systems. It means that NH_2^- and OH^- may be interchanged in many compounds and similarly =NH group is analogous to =O group. The analogy of H_2O and NH_3 systems are given by the following examples :

	Properties	*H_2O system*	*NH_3 system*
1.	Ionization	$H^+ + OH^-$ or $H_3O^+ + OH^-$	$H^+ + NH_2^-$ $NH_4^+ + NH_2^-$(liq.)
2.	Base	KOH	KNH_2
3.	Acid	HCl or $H_3O^+Cl^-$	$NH_4^+Cl^-$
4.	Solvolysis	$Mg(OH)Cl$ (hydrolysis)	$Hg(NH_2)Cl$ (ammonolysis)
5.	Solvates	$CaCl_2.2H_2O$	$CaCl_2.2NH_3$
6.	Neutralization	$KOH + H_3O^+Cl^- = KCl + 2H_2O$	$KNH_2 + NH_4Cl = KCl + 2NH_3$
7.	Hydrogen bond	Strong H—OH bond	Weak H—NH bond

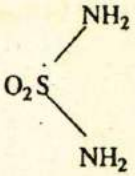
Thus the replacement of – OH by $-NH_2$ gives the following products in acids :—



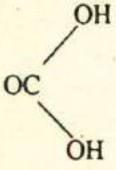
sulphuric acid



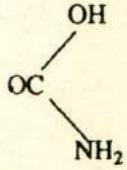
sulphamic acid



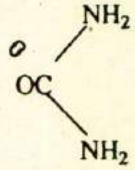
sulphamide



carbonic acid

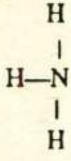


carbamic acid

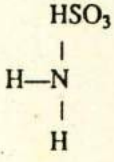


carbamide (urea)

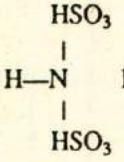
Similarly,



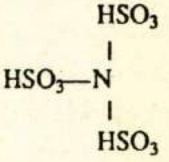
ammonia



amidosulphonic acid



imidosulphonic acid



nitrilosulphonic acid

(5) Other properties of ammonia may be given by the following equations:—

(a) $2NH_3 + 3CuO \xrightarrow{heat} N_2 + 3Cu + 3H_2O$

(b) $2NH_3 + 3Mg \xrightarrow{heat} Mg_3N_2 + 3H_2$

(c) $4NH_3 + 3\,O_2 \xrightarrow{burns} 2N_2 + 6H_2O$

(d) $4NH_3 + 5\,O_2 \xrightarrow[Pt\ catalyst]{700°C} 4NO + 6H_2O$

(e) $8NH_3 + 3Cl \longrightarrow 6NH_4Cl + N_2$

Liquid ammonia : Liquid ammonia is an associated solvent like water. But HNH bond in NH_3 is weaker than HOH bond in H_2O. The property of NH_3 as an associated solvent is less pronounced than H_2O. But liquid NH_3 possesses the

ability to dissolve many alkali and alkaline earth metals. The free metals can be recovered by evaporation of ammonia. The alkali metals dissolve in liquid NH_3 giving blue solution without the evolution of H_2. The blue colour is due to ammoniated electron.

$$K + Liq\ NH_3 \rightarrow K + e^-(NH_3)$$

But H_2O gives H_2 :

$$Na + H_2O \rightarrow NaOH + H_2$$

This is due to the reduction :

$$2H_3O^+ + 2e \rightarrow 2H_2O + H_2$$

Dilute solutions of Na and other metals in liquid ammonia are blue in colour and concentrated solutions have bronze colour. They conduct electricity like metals. It is believed that free electrons are present in the solution as solvated products :

$$Na = Na^+ + e^-$$

$$Na^+ + xNH_3 \rightleftharpoons Na(NH_3)_x^+$$

$$e^- + yNH_3 \rightleftharpoons e^-(NH_3)_y$$

Evaporation of a solution of metal in liquid ammonia gives the original metal. In presence of catalyst liquid ammonia solution of alkali metal gives H_2 because of the reaction.

$$2K + 2NH_3 \rightarrow 2KNH_2 + H_2$$

Ammonium Salts

General properties : All ammonium salts containing univalent NH_4^+ radical behave like alkali metals salts. NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3, i.e., salts of strong acids, closely resemble alkali metal salts. The size of NH_4^+ 1.48 Å is almost the same as that of Cs^+ ion and a little larger than K^+ ion (1.33 Å). All ammonium salts are very soluble in water except the following :—

$$NH_4ClO_4 \qquad (NH_4)_3[Co(NO_2)_6] \qquad (NH_4)_2PtCl_6$$

NH_4- salts of strong acids are slightly hydrolysed in water but those of weak acids, such as carbonate, acetate, cyanides etc., are very much hydrolysed :

$$NH_4CN + H_2O \rightleftharpoons NH_4OH + HCN$$

When NH_4- salts of non-oxidizing acids are heated they decompose to give NH_3 and acids in gaseous states :

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

$$NH_4HCO_3 \rightleftharpoons NH_3 + H_2CO_3$$

$$\Downarrow$$

$$CO_2 + H_2O$$

But NH_4- salts of oxidizing acids give N_2 or N_2O

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O$$

$$NH_4NO_3 = N_2O + 2H_2O$$

Some of the important ammonium salts are described here.

(1) ***Ammonium sulphate,*** $(NH_4)_2SO_4$: The ammonical liquor obtained from the manufacture of coal gas is decomposed by lime and the liberated ammonia and steam is passed through dil H_2SO_4 to give $(NH_4)_2SO_4$. The synthetic ammonia is also absorbed in H_2SO_4 to produce $(NH_4)_2SO_4$.

This is also obtained when NH_3 gas and CO_2 are passed through powdered gypsum, $CaSO_4$, suspended in water :

$$CaSO_4 + 2NH_3 + CO_2 + H_2O = (NH_4)_2SO_4 + CaCO_3$$

$(NH_4)_2SO_4$ is largely used as a fertilizer and for making other NH_4- salts. It is rapid action fertilizer and supplies N_2 to the plants at a rapid rate.

(2) ***Ammonium nitrate,*** NH_4NO_3 : This is prepared by passing NH_3 gas in HNO_3 and also by double decomposition between $NaNO_3$ and $(NH_4)_2SO_4$:

$$2NaNO_3 + (NH_4)_2SO_4 = 2NH_4NO_3 + Na_2SO_4$$

NH_4NO_3 is used in explosives. NH_4NO_3 with Al powder known as *Ammonal* and NH_4NO_3 mixed with T.N.T. known as *Amatol* are high explosives.

(3) ***Ammonium chloride,*** NH_4Cl : This is much used in the laboratory as a reagent. This is obtained when $(NH_4)_2SO_4$ is boiled with NaCl solution and also by absorbing NH_3 gas in HCl.

NH_4Cl dissociates on heating to $NH_3 + HCl$:

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

It is for this reason that NH_4Cl is used as a flux in soldering because it cleans the oxide-coated surface of the metal :

$$CuO + 2NH_4Cl = CuCl_2 + 2NH_3 + H_2O$$

It is also used in dry, cells.

(4) ***Ammonium phosphate,*** $(NH_4)_3PO_4$: The normal $(NH_4)_3PO_4$ is actually formed from $(NH_4)_2HPO_4$ when the aqueous solution of $(NH_4)_2HPO_4$ is saturated with NH_3 gas. On evaporating H_3PO_4 which has been saturated with NH_3 gas, the compound which crystallises out, is $(NH_4)_2HPO_4$. The controlled neutralization of H_3PO_4 with NH_3 produces $NH_4H_2PO_4$. DAP which is diammonium-phosphate $(NH_4)_2HPO_4$ is used as fertilizer.

Ammonium phosphate is used as fertilizer and for fire-proofing of timber.

Microcosmic salt is $NaNH_4HPO_4.H_2O$. When Na_2HPO_4 and $(NH_4)_2HPO_4$ in the ratio of $\frac{5}{2}$ are mixed in aqueous solution and crystallised, the crystals consist of $NaNH_4HPO_4.H_2O$. The sparingly soluble microcosmic salt is also formed when Na_2HPO_4 and NH_4Cl are mixed together in molar proportions in aqueous solution and crystallized.

Microcosmic salt is used for identification of metals and also silica in qualitative analysis as in the case of borax bead test. The microcosmic salt forms colourless bead on a platinum wire and becomes coloured with a trace of metal oxide due to the formation of coloured metal phosphate. Silica gives the familiar skeleton-like mass with this salt in a similar manner.

(5) Ammonium carbonate, $(NH_4)_2CO_3$: When NH_4Cl or $(NH_4)_2SO_4$ is heated with $CaCO_3$ the product is $(NH_4)_2CO_3$. This is extensively hydrolysed in water and even in the solid state it smells of NH_3. Some ammonium carbamate is also formed during the reaction :

$$(NH_4)_2CO_3 \rightleftharpoons NH_2COONH_4 + H_2O$$

(6) ***Ammonium sulphide,*** $(NH_4)_2S$: When H_2S is passed in aqueous NH_3 the first product is NH_4HS, but at lower temperature and excess of NH_3

the normal salt $(NH_4)_2S$ is formed. It is also extensively hydrolysed and easily decomposed in the solid state to NH_3 and H_2S.

Yellow ammonium sulphide is obtained when H_2S is passed in NH_4OH to which fine powder of sulphur has been suspended. The yellow ammonium sulphide has a yellow colour and contains a polymer having —S—S—S— chain. This composition is generally expressed as $(NH_4)_2Sx$. This is used in qualitative analysis because it dissolves sulphides of As, Sb, Sn forming thio-salts from which the sulphides are precipitated by adding dilute acids.

Ammonium amalgam : When ammonium salts are electrolysed with a Hg cathode, the metallic mercury is supposed to contain free NH_4^+ ion which is stabilized in Hg by incorporating an extra electron. It is difficult to arrive at any conclusive picture about the free NH_4^+ ion in Hg except as an alloy, i.e., NH_4—Hg.

Hydrazine. N_2H_4

Hydrazine is another hydride of nitrogen. This is obtained by the following methods :—

1. On oxidizing NH_3 by NaOCl in presence of alkali and gelatine or glue which prevent side reactions :

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$$

$$NH_3 + NH_2Cl + NaOH \rightarrow N_2H_4 + NaCl + H_2O$$

Chloramine, NH_2Cl, is an intermediate compound. N_2H_4 remains in the solution and is crystallised as hydrazine sulphate, $N_2H_4.H_2SO_4$, or chloride, $N_2H_4.HCl$, by adding respective acids. When these crystals are distilled with KOH under reduced pressure, $N_2H_4.H_2O$ is obtained as distillate.

2. By reducing nitric oxide with Na—Hg in presence of saturated solution of K_2SO_3 :

$$2NO + 8H = N_2H_4.H_2O + H_2O$$

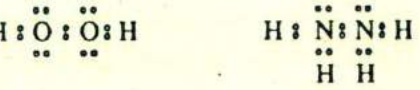
$$N_2H_4.H_2O + BaO = N_2H_4 + Ba(OH)_2$$

$$N_2H_4.HCl + CH_3ONa = N_2H_4 + CH_3OH + NaCl$$

Hydrazine is a fuming liquid, boiling point being 114°C. Anhydrous N_2H_4 is thermally stable but highly reactive. The free base is not obtained by the

action of alkali on acid salts, such as $N_2H_4.HCl$ but the reaction always gives $N_2H_4.H_2O$:

N_2H_4 may be regarded as the analogous of H_2O_2 with which it is isoelectronic. Hydrazine may thus be regarded as a difunctional amine, $NH_2.NH_2$:



Properties of N_2H_4 : (1) On heating, N_2H_4 is decomposed into ammonia and N_2 :

$$N_2H_4 = N_2 + 4NH_3$$

(2) It burns in air and reacts vigorously with halogens :

$$N_2H_4 + O_2 = N_2 + 2H_2O$$

$$N_2H_4 + 2Cl_2 = ClHN{-}NHCl + 2Cl^-$$

$$\downarrow$$

$$N_2 + 2HCl$$

(3) Aqueous N_2H_4 is weakly basic :

$$N_2H_4 + H_3O^+ = \underset{\text{Hydrazinium ion}}{N_2H_5^+} + H_2O$$

$$N_2H_4 + HCl = N_2H_5^+ + Cl^-$$

$$Zn^{+2} + 4N_2H_4 = Zn(N_2H_4)_4^{+2}$$

$$CH_3Br + N_2H_4 = \underset{\text{Nucleophilic displacement on carbon}}{CH_3NHNH_2} + HBr$$

N_2H_4 is a reducing agent. "One electron" oxidizing agent, such as Fe^{+3} and Ce^{+4}, Cu^{+1} or halogens yield N_2. In basic solution, the yield of N_2 is quantitative. The quantitative reaction with iodine can be used to determine hydrazine :

N_2H_4 thus behaves as a good reducing agent and a base.

$$N_2H_4 + 2I_2 = N_2 + 4HI$$

The reaction of N_2H_4 with H_2O_2 (both liquids) gives N_2 and steam (both gases) with high liberation of energy accompanied by tremendous increase in volume and the mixed liquids have been used as rocket fuels:

$$N_2H_4 + 2H_2O_2 = N_2 + 2H_2O$$

Hydrazoic acid, HN_3, and Azides

Hydrazoic acid or azoimide, HN_3, contains 98% N_2 and is explosive in the pure state. It can be studied in aqueous solutions. HN_3 can be prepared as follows:—

(1) The sodium salt, sodium azide, NaN_3, can be prepared by nucleophilic attack on N_2O with sodamide :

$$NaNH_2 + N_2O = NaN_3 + H_2O$$

(2) By the action of HNO_2 on $N_2H_4.HCl$:

$$N_2H_4.HCl + NaNO_2 = N_2H_4.HNO_2 + NaCl$$

$$N_2H_4.HNO_2 \rightarrow HN_3 + 2H_2O$$

(3) By the action of NCl_3 on N_2H_4 :

$$N_2H_4 + NCl_3 = HN_3 + 3HCl$$

Properties of hydrazoic acid : It is a colourless smelling liquid and detonates violently on shock. It is a weak acid and reacts with both oxidizing and reducing agents :

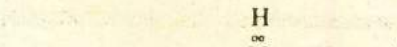
$$HN_3 + 4H_2 = 3NH_3$$

$$2HN_3 + O = 3N_2 + H_2O$$

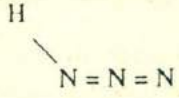
Azides : Metals, like Zn, Fe, Al, Mg, Hg and Pb react with HN_3 giving azides. With Mg, H_2 is also liberated but other metals give NH_3 and other nitrogen compounds :

The azides are unstable compounds and some of them are used as explosives. $Pb(N_3)_2$ (lead azide) is used as a detonator for military explosives.

The linear structure of HN_3 and also the azide ion N_3^- has been proved :



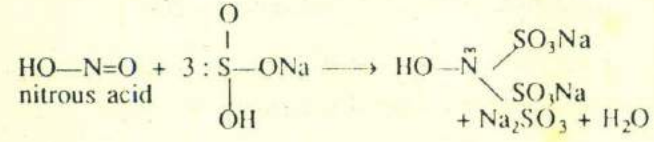
The three atoms of N in the azide ions also lie in the same straight line. H is not is the same line and the formula can be written as,

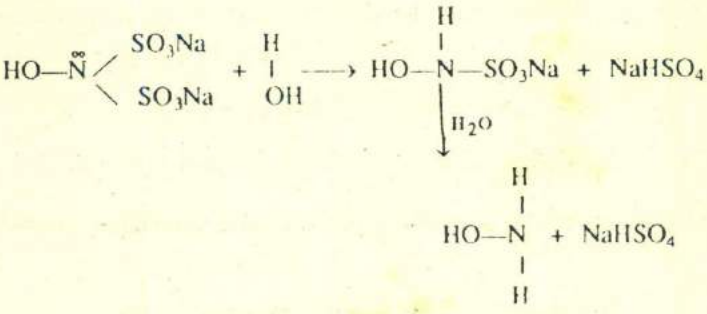


Hydroxylamine, NH_2OH

Hydroxylamine, NH_2OH, may also be regarded as a nitrogen analogue of H_2O_2 or a derivative of ammonia. It is prepared by the following methods :—

(1) Hydroxylamine is prepared by the reduction of HNO_2 with H_2SO_3. It is an example of reduction-reaction that proceeds in shifts of two electrons by formation and breakage of covalent bonds. In actual practice, $NaNO_2$ is reduced by SO_2 in presence of Na_2CO_3 at low temperature. Sodium salt of hydroxylamine sulphonic acid is first formed which on hydrolysis gives NH_2OH:





(2) Electrolytic reduction of nitric acid also gives NH_2OH. The reduction of HNO_3 occurs at the cathode. HNO_2 is first formed which is reduced to NH_2OH :

$$HNO_3 + 2H = HNO_2 + H_2O$$

$$HNO_2 + 4H = NH_2OH + H_2O$$

(3) When NO is reduced with Sn + conc HCl :

$$NO + 3H = NH_2OH$$

(4) Ethyl nitrate on reduction with Sn + HCl :

$$C_2H_5NO_3 + 6H = NH_2OH + H_2O + C_2H_5OH$$

NH_2OH prepared by the above methods is an aqueous solution. Anhydrous NH_2OH can be prepared by the following processes :—

(1) By the reaction of hydroxylamine hydrochloride with sodium methoxide in alcoholic solution :

$$NH_2OH.HCl + CH_3ONa = NH_2OH + NaCl + CH_3OH$$

NH_2OH is somewhat soluble in alcohol and is separated from insoluble NaCl. Methyl alcohol is removed by distillation under reduced pressure.

(2) Hydroxylamine phosphates on heating gives NH_2OH :

$$(NH_2OH)_3.H_3PO_4 \longrightarrow 3NH_2OH + H_3PO_4$$

Properties of NH_2OH : (1) It is needle-like white solid, melting point 33°C. It is soluble in water and in ether. It is thermally unstable.

(2) It is an active reducing agent and reacts violently with halogens and other powerful oxidizing agents :

$$2NH_2OH + 2Cl_2 = N_2O + H_2O + 4HCl$$

$$2NH_2OH + 4FeCl_3 = 4FeCl_2 + N_2O + H_2O + 4HCl$$

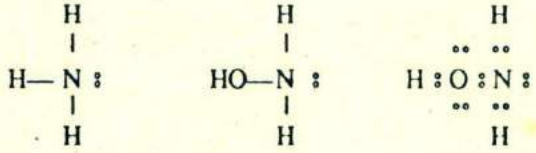
(3) NH_2OH also acts as an oxidizing agent in alkaline medium evolving NH_3 :

$$NH_2OH + 2Fe(OH)_2 + H_2O = 2Fe(OH)_3 + NH_3$$

(4) Like hydrazine, NH_2OH forms salts with HCl and H_2SO_4 and are available in these forms :

$$NH_2OH.HCl \qquad NH_2OH.H_2SO_4$$

These compounds are examples of addition compounds. NH_2OH may be considered as a derivative of NH_3 in which one H has been replaced by OH :



Nitrogen halides : There are no direct reactions between N_2 and halogens. Only NF_3 and NCl_3 are known. NBr_3 or NI_3 are doubtful compounds. But $NH_3(NX_3)$ type of compounds are formed with Br_2 and I_2(X=Br or I).

NF_3 is obtained by the reaction of NH_3 and F_2 :

$$NH_3 + F_2 \longrightarrow NH_2F + HF$$

$$NH_2F + F_2 \longrightarrow NHF_2 + HF$$

$$NH_2F + F_2 \longrightarrow NF_3 + HF$$

Electrolysis : $NH_4HF_2 + 12F = 2NF_3 + 10HF$

NF_3 is a colourless poisonous gas and a very stable molecule. It reacts with steam :

$$2NF_3 + 3H_2O = 6HF + NO_2 + NO$$

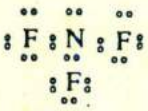
NCl_3 is a highly explosive compound. It is obtained by the reaction of Cl_2 with NH_4Cl or NH_3 and also by the action of HOCl on NH_3 :

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl$$

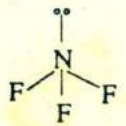
$$NH_3 + 3HOCl = NCl_3 + 3H_2O$$

NCl_3 is an oily liquid and explodes violently even on exposure to light.

The stability in the case of NF_3 has been attributed to the partial ionic bonding between N and F although NCl_3 and NF_3 both are shown to have covalent bond using the tetrahedral sp^3 bonds of nitrogen :



Lewis structure



Tetrahedral structure

In effect, NCl_3 and NF_3 have pyramidal shapes. The energy released on breaking the NCl_3 bond is tremendous :

$$2NCl_3 = N_2 + 3Cl_2 + 111 \text{ Kcal}$$

Oxides of Nitrogen

Nitrogen froms oxides having oxidation state from +1 to + 6. Some of the important oxides are given in Table 20.3 indicating their formula, name, structures and reactivities. The structures given do not represent the actual distributions of electrons but give only the total number of electrons involved in the formation of the molecules. Molecules having unpaired electrons must, as a rule, show the resonance structure due to the shifts of the electrons from the paired to unpaired state.

Nitrous oxide, N_2O : (i) When ammonium nitrate, NH_4NO_3, is gently heated, nitrous oxide, N_2O, is formed :

$$NH_4NO_3 = N_2O + 2H_2O$$

This is oxidation-reduction reaction in which N of NH_4^+ is oxidized by N in the NO_3^- ion. The heating of NH_4NO_3 must be gentle, otherwise explosion may occur.

(ii) N_2O is also obtained from NH_2OH being oxidized with $NaNO_3$, $CuSO_4$, $FeCl_3$ etc :

$$NH_2OH + HNO_2 = N_2O + 2H_2O$$

(iii) N_2O is also formed when Zn reacts with dil HNO_3 :

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 5H_2O + N_2O$$

N_2O is a colourless gas with pleasant taste and odour and when inhaled it produces hysterical laughter. Hence its name is *laughing gas*. N_2O is isoelectronic with CO_2 with which it forms mixed crystals. N_2O does not react with H_2O or alkalies. However, hyponitrous acid, $H_2N_2O_2$, gives N_2O on dehydration.

N_2O is not very reactive but has the tendency to release N_2 and O_2, which gives it reactivity when heated. N_2O then reacts with S and P in the heated condition :

$$S + 2N_2O = SO_2 + 2N_2$$

N_2O is oxidized to NO by strong oxidizing agents, such as $KMnO_4$.

Table 20·3. Oxides of Nitrogen.

Formula	*Structures*	*Oxn. states of N*	*Name*	*Colour*	*Reactivity*
N_2O	$N \equiv N \rightarrow O$	+1	Nitrous oxide	Colourless gas	Uureactive
NO	$\dot{N}=O$ or $N=\dot{O}$	+2	Nitric oxide	Colourless gas	Reactive
N_2O_3	$O=N-O-N=O$	+3	di-Nitrogen trioxide	Blue solid	Dissociated as gas
NO_2	$O \leftarrow N \rightarrow O$	+4	Nitrogen peroxide	Brown gas	Reactive
N_2O_4	$O = N \rightarrow O$ $\quad\quad\quad

Nitric oxide, NO : There are various ways of preparing NO :—

(i) Heating Cu turnings with conc HNO_3 :

$$3\,Cu + 8NHO_2 = 2NO + 3\,Cu(NO_3)_2 + 4H_2O$$

(ii) Pure NO is obtained by heating $FeSO_4$ with KNO_3 and H_2SO_4 :

$$2KNO_3 + 6FeSO_4 + 4H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + 2NO + 4H_2O$$

(iii) By the reaction of $NaNO_2$ and KI in presence of H_2SO_4, pure NO is obtained :

$$2NaNO_2 + 3H_2SO_4 + 2KI = 2NaHSO_4 + K_2SO_4 + 2NO + 2H_2O + I_2$$

(iv) N_2 and O_2 combine in the arc process in presence of platinum. NH_3 may also be oxidized to NO :

$$N_2 + O_2 = 2NO \qquad 2NH_3 + 5\,O_2 = 4NO + 6H_2O$$

NO is a colourless gas but rapidly takes up O_2 from the air to form NO_2 which is brown-red. The reaction is reversible at room temperature.

$$2NO + O_2 \rightleftharpoons 2NO_2 \text{ or } N_2O_4$$

NO is readily absorbed in $FeSO_4$ solution forming intensely brown solution, $FeSO_4.NO$ or $[Fe(NO)]^{+2}$ ions actually $[Fe(NO)(H_2O)_5]^{+2}$ with is used in NO_3^- test.

NO acts both as a reducing agent and an oxidizing agent. Thus NO oxidize H_2SO_3 to H_2SO_4 :

NO is oxidized by $KMnO_4$ solution to HNO_3.

NO is an odd molecule and has an unpaired electron :

$$:\tilde{\underset{\cdot}{N}}:\,:\mathring{\underset{\cdot}{O}}: \qquad\qquad :\mathring{\underset{\cdot}{N}}:\,:\tilde{\underset{\cdot}{O}}:$$

NO easily forms nitrosonium or nitrosyl ion (NO^+) by losing the odd electron as in the case of NO^+Cl^- (nitrosyl chloride), $NO^+HSO_4^-$ (nitrosonium bisulphate), $NO^+ ClO_4^-$ (nitrosyl perchlorate).

Odd molecules are defined as molecules containing odd number of electrons in their outer electron level, such as NO (5+6=11) and NO_2 (5+12=17). The odd

unpaired electron is not confined to a specific orbital of nitrogen or oxygen atom in NO but it is said to be "delocalized". The unpaired electron is present in an orbital which is combined to both N and O.

Dinitrogen trioxide, N_2O_3 : When a mixture of one part of NO and one part of NO_2 is cooled, it becomes a blue liquid at -21°C and freezes to a blue solid. On warming the equilibrium gas mixture is again formed :

$$N_2O_3 \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} NO + NO_2$$

It is also obtained by the action of HNO_3 on As_2O_3 :

$$As_2O_3 + 2HNO_3 = As_2O_5 + H_2O + N_2O_3$$

When N_2O_3 gas is passed into aqueous KOH, the product is KNO_2 :

$$N_2O_3 + 2KOH = 2KNO_2 + H_2O$$

The structure is ambiguous containing both ONONO and N—N bonds. N_2O_3 is an acidic oxide being the anhydride of HNO_2.

Nitrogen peroxide, NO_2 : NO_2, and Nitrogen tetroxide, N_2O_4 : NO_2 is prepared by heating $Pb(NO_3)_2$:

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

When Cu reacts with very concentrated HNO_3 in the heated condition, NO_2 is evolved :

NO_2 is commercially formed when NO is exposed to air as the deep brown coloured gas :

$$2NO + O_2 = 2NO_2$$

At ordinary temperature NO_2 is in equilibrium with its dimer, N_2O_4, but at the higher temperature N_2O_4 is dissociated into NO_2 :

$$2NO_2 \rightleftharpoons N_2O_4$$

N_2O_4 is a colourless gas. In the solid state and at low temperature N_2O_4 predominates since it is colourless. At higher temperature the colour becomes intense brown because of predominance of NO_2 :

NO_2 is absorbed in alkalis to form both nitrites and nitrates :

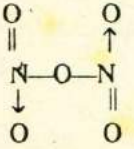
$$2NO_2 + H_2O = HNO_2 + HNO_3$$

NO_2 is an acidic oxide.

NO_2 also contains an odd number of electron. The resonance forms are :



N_2O_5 is represented as



OXYACIDS OF NITROGEN

Nitrogen forms a series of oxyacid. The most important of these are the following :—

1. Nitric Acide, HNO_3.

2. Nitrous Acid, HNO_2.

3. Hyponitrous Acid, HNO or $H_2N_2O_2$.

Nitric acid, HNO_3

Nitric acid is one of the most important chemicals for industrial use. It has been manufactured from $NaNO_3$ or KNO_3 since the days of alchemists. Now-a-days other methods for the manufacture of HNO_3 have been developed. Generally, the following methods are used for large-scale production of HNO_3.

(i) **From nitrates** : HNO_3 was produced commercially by heating a mixture of $NaNO_3$ and conc H_2SO_4. The charge of $NaNO_3$ and H_2SO_4 is taken in cast iron retorts and heated to about 200°C when HNO_3 is distilled off :

$$NaNO_3 + H_2SO_4 \rightleftharpoons NaHSO_4 + HNO_3$$

At ordinary temperature the reaction is reversible and an equilibrium is established. But HNO_3 boils at 83°C and H_2SO_4 boils at 338°C and the solid $NaNO_3$ are not volatile, the HNO_3 formed is readily distilled. The distillate is passed through water-cooled silica tubes to condense the conc HNO_3 first. Fumes of HNO_3 escaping condensation is scrubbed with cold water and collected as dilute HNO_3. The yellow colour of HNO_3 is due to dissolved NO_2 and is removed by distillation in vacuum.

(ii) From air (Arc process) : Air (which contains mainly N_2 and O_2) is subjected to high tension electric discharge or passed through an arc at temperature of above 3000°C. N_2 and O_2 combine to give NO.

$$N_2 + O_2 \rightleftharpoons 2NO - 43.2 \text{ Kcal}$$

The endothermic reaction gives only about 5% conversion at 3000°C. On cooling NO combines with more O_2 to form NO_2 :

$$2NO + O_2 = 2NO_2$$

The brown fumes of NO_2 is washed with water on counter current principle, i.e., the gases and vapours going upward and water trickling downward in quartz vessel :

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

$$NO + NO_2 + H_2O = 2HNO_2$$

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

The escaping gases may contain some NO and NO_2 and are absorbed in alkali solutions to produce $NaNO_2$:

$$NO + NO_2 + Na_2CO_3 = 2NaNO_2 + CO_2$$

This is one of the processes for the fixation of atmospheric nitrogen. The high cost of electricity and low yield of HNO_3 has led to the discontinuation of the process.

It has been estimated that in nature about 40 million tons of nitrogen is fixed annually as a result of electric discharge during lightning and other photochemical phenomena.

(iii) From ammonia (Ostwald's Process) : This process consists of the oxididation of ammonia to NO and NO to NO_2 which with water gives HNO_3. Ammonia mixed with 10 times its volume of air and heated to 600°C is passed through a converter containing platinum gauze which acts as a catalyst. NH_3 is oxidized to NO :

$$4NH_3 + 5\,O_2 = 4NO + 6H_2O + 215\ Kcal$$

The exothermic reaction proceeds without supply of heat except the initial heating. About 90% of NH_3 is converted to NO. Additional air is admitted to cool the mixture and oxidize NO to NO_2 :

$$2\,NO + O_2 = 2NO_2 + 27.8\ Kcal$$

The mixed gases containing NO, NO_2, unreacted N_2 and O_2 etc. are passed in an absorption tower on counter current principle where HNO_3 is formed :

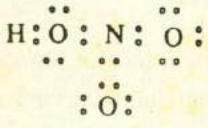
$$3NO_2 + H_2O = 2\,HNO_3 + NO$$

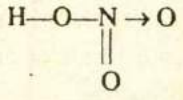
NO is returned to absorption tower with more air.

Pure HNO_3 is made by distillation of the product under reduced pressure and passing ozone to the distillate. Distillation of an aqueous solution of HNO_3 leads to a constant boiling mixture when the concentration of HNO_3 is 68.4% at 122°C. Pure HNO_3 is obtained from this mixture by distillation in presence of H_2SO_4.

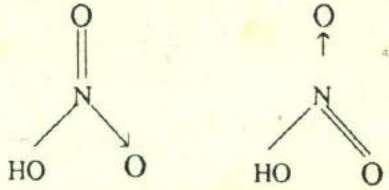
Fuming HNO_3 is a red liquid and is made by bubbling NO_2 gas into concentrated HNO_3. Fuming HNO_3 reacts more vigorously with many substances.

Properties of HNO_3 : It is a fuming liquid, miscible with water and has a high vapour pressure. Concentrated acid gives off NO_2 by light and heat. Nitric acid has the following electronic formula :—

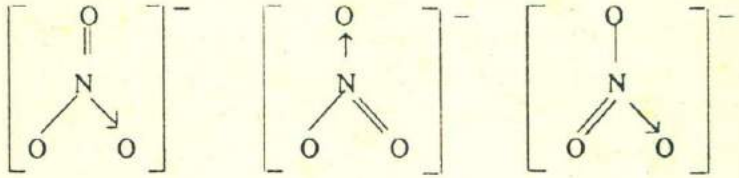




In fact, NO_3 group of HNO_3 has a triangular arrangement and has a resonating structure :



The NO_3^- ion, therefore, has three different contributing structures :



The unstable nature of HNO_3 is shown by its decomposition to NO_2 and O_2 when heated :

$$4\ HNO_3 = 4\ NO_2 + O_2 + 2H_2O$$

Nitric acid exhibits three types of properties : (a) Acid properties, (b) Oxidizing agent, (c) Nitrating agent.

(a) HNO_3 as an acid : This is illustrated by the following equations : When nitric acid reacts with bases, such as metal oxides, hydroxides and carbonates to produce metal nitrates and water. In dilute solution HNO_3 is completely dissociated into H^+ ions and NO_3^- ions. Hence HNO_3 in dilute solutions behaves as an acid. Thus,

$$CuO + 2\ HNO_3 = Cu(NO_3)_2 + H_2O$$

$$Mg(OH)_2 + 2\ HNO_3 = Mg(NO_3)_2 + 2H_2O$$

$$CaCO_3 + 2\ HNO_3 = Ca(NO_3)_2 + H_2O + CO_2$$

With Mg and some sulphides in dilute solution, it evolves H_2 or H_2S as the case may be :

$$Mg + 2\ HNO_3 = Mg(NO_3)_2 + H_2$$

$$MnS + 2\ HNO_3 = Mn(NO_3)_2 + H_2S$$

(b) HNO_3 as an oxidizing agent : Nitric acid is a powerful oxidizing agent. The reduction products of HNO_3 are N_2 or one or more of the nitrogen compounds, such as N_2O, NO, NO_2, NH_3. This depends upon three factors : (i) Acid concentration ; (ii) nature of the reducing agents ; (iii) temperature of the reactions.

The oxidizing actions of HNO_3 may be classified according to the nature of reducing agent as follows :—

(a) Action of HNO_3 on metals : In dilute solution with possibly Mg only, HNO_3 behaves as an acid liberating H_2. But with other metals the oxidizing actions predominate. Au and Pt do not react with HNO_3 under any condition. Although the reduction products may be a mixture of nitrogen compounds, but for the sake of simplicity the following points may be remembered for writing the equations :

HNO_3 in extremely dilute solutions gives NH_3. (Change of oxidation number of N from +5 to −3).

HNO_3 in very dilute solutions gives N_2O (Change of oxidation number of N from +5 to +1).

HNO_3 in dilute solution gives NO (Change of oxidation number of N from +5 to +2).

HNO_3 in concentrated solution and hot condition gives NO_2 (Change of oxidation number of N from +5 to +4).

HNO_3 vapour passed over red-hot metal gives N_2 (Change of oxidation number of N from +5 to 0).

(i) Zn, Fe and Sn with extremely dilute HNO_3 in the cold give NH_3 which combines with excess HNO_3 to form NH_4NO_3 :

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3$$

$$4Sn + 10HNO_3 = 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3$$

(ii) Zn reacts with very dilute HNO_3 in the cold to give N_2O :

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + N_2O + 5H_2O$$

(iii) In the ordinary conditions the dilute HNO_3 always produces NO. This is the most common reaction product of HNO_3 with metals in dilute conditions (moderately) and also whenever HNO_3 acts with any substance in aqueous solutions :

$$3\,Cu + 8\,HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O$$

With Hg, NO is formed. Dilute HNO_3 gives $Hg_2(NO_3)_2$ but conc HNO_3 gives $Hg(NO_3)_2$.

(iv) In concentrated and hot condition most metals react with HNO_3 to give NO_2 :

$$Cu + 4\,HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$Fe + 6\,HNO_3 = Fe(NO_3)_2 + 3NO + 3H_2O$$

(v) When HNO_3 in the vapour form is passed over heated Cu nitrogen gas is evolved :

$$5Cu + 10\,HNO_3 \rightarrow 5Cu(NO_3)_2 + 6H_2O + N_2$$

$Cu(NO_3)_2$ formed may also be decomposed to CuO and NO_2.

Passive condition :

Some of the metals in concentrated HNO_3 are rendered *Passive* and no action takes place with Fe, Cr, Ni, Co and even Al. This happens particularly when the metals are pure and HNO_3 is also pure. Impurities in metals and in HNO_3 produce vigorous reactions possibly due to the electron transfer by setting up miniature galvanic cells.

(b) Action of HNO_3 on non-metals : Non-metals, such as S, C, I_2, etc. are oxidized by concentrated HNO_3 in the hot condition evolving NO_2 and the oxyacids or oxides of the non-metals :

$$C + 4HNO_3 \quad CO_2 + 4NO_2 + 2H_2O$$

$$S + 4HNO_3 = H_2SO_4 + 6NO_2 + 2H_2O$$

$$P + 5HNO_3 = H_3PO_4 + 10NO_2 + H_2O$$

$$I_2 + 10HNO_3 = 2HIO_3 + 10NO_2 + 4H_2O$$

(c) Action of HNO_3 on compounds in solutions : In aqueous solutions HNO_3 is always converted to NO :

$$3H_2S + 2HNO_3 = 3S + 2NO + 4H_2O$$

$$3Fe^{+2} + HNO_3 + 3H^+ = 3Fe^{+3} + NO + 2H_2O$$

But compounds when heated with concentrated HNO_3 give NO_2 :

$$SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2$$

$$PbS + HNO_3 \rightarrow Pb(NO_3)_2 + PbSO_4 + NO_2$$

$$CuS + 8HNO_3 = CuSO_4 + 8NO_2 + 4H_2O$$

There are some metals like Au and Pt and also compounds, such as HgS, which are not oxidized by HNO_3 at all. Such substances can be oxidized by means of a mixture of HNO_3 and HCl in volume ratio of 1 : 3. The mixture is known as *Aqua Regia*. HNO_3 oxidizes HCl to form Cl_2 and NOCl (nitrosyl chloride). The formation of chlorocmplexes of the metal facilitates the reactions :

$$HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2$$

$$HgS \rightleftharpoons Hg^{+2} + S^{-2}$$

$$Hg^{+2} \xrightarrow{4Cl^-} HgCl_4^{-2}$$

$$S^{-2} \xrightarrow{2HNO_3} S + NO_2 + H_2O$$

(d) Nitration reactions of HNO_3 : These reactions generally take place with organic compounds. Thus, nitration of glycerine is carried out with HNO_3 mixed with H_2SO_4 to absorb the H_2O formed :

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(NO_3)_3 + 3H_2O$$

The reaction of HNO_3 with H_2SO_4 produces NO_2^+ cations which reacts with organic molecules by an atom or group of atoms originally present. Thus, TNT is formed by nitrating toluene in presence of H_2SO_4 :

$$CH_3C_6H_5 + 3HNO_3 = CH_3C_6H_2(NO_2)_3 + 2H_2O$$

Uses of HNO_3 : (1) It is used as an active oxidizing agent. (2) Manufacture of explosives, T. N. T., dyes, plastics, drugs etc. (3) Nitrates are used as fertilizers.

Nitrous acid, HNO_2

HNO_2 is obtained in solution only. Pure HNO_2 has not been isolated because it is unstable. Even in solution it decomposes to form HNO_3 and NO :

$$3HNO_2 = HNO_3 + 2\,NO + H_2O$$

It is obtained by dissolving N_2O_3 in water at ice-cold temperature :

$$N_2O_3 + H_2O = 2\,HNO_2$$

HNO_2 is formed when $Ba(NO_2)_2$ is treated with H_2SO_4 :

HNO_2 is a weak acid in solution. It acts as an *oxidizing agent* towards strong reducing agents and also as a *reducing agent* in presence of active oxidizing agents. HNO_2 itself cannot be isolated from solution since it decomposes easily.

$NaNO_2$ or KNO_2 in H_2SO_4 has the same action as HNO_2 solution. Hence, whenever HNO_2 is required it is used in the form of $NaNO_2$.

HNO_2 is oxidized by $KMnO_4$ or H_2O_2 or halogens :

$$2KMnO_4 + 3H_2SO_4 + 5NaNO_2 = K_2SO_4 + 2MnSO_4 + 2H_2O + 5NaNO_3$$

$$H_2O_2 + NaNO_2 = NaNO_3 + H_2O$$

$$Br_2 + NaNO_2 + H_2O = NaNO_3 + 2HBr$$

HNO_2 oxidizes KI to I_2 in presence of acid :

$$2KI + 2HNO_2 + H_2SO_4 = I_2 + 2NO + 2H_2O + K_2SO_4$$

$SnCl_2$ is oxidized to $SnCl_4$:

$$SnCl_2 + 2NaNO_2 + 4HCl = SnCl_4 + 2H_2O + 2NO + 2NaCl$$

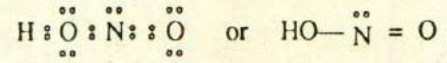
$$H_2S + 2NaNO_2 + H_2SO_4 = S + 2NO + Na_2SO_4 + 2H_2O$$

Sodium nitrite, $NaNO_2$, is produced from $NaNO_3$ by heating with Pb or coke :

$$NaNO_3 + Pb \rightarrow NaNO_2 + PbO$$

$$NaNO_3 + C \rightarrow NaNO_2 + CO$$

HNO_2 has the structure :



The presence of unshared pair on the nitrogen imparts basic and reducing properties to HNO_2. The N = O double bond gives the acid and oxidizing properties. $-NO_2$ ion is also a coordinating agent and coordinates as — ONO in some cases as in $Na_2Co(NO_2)_6$.

$NaNO_2$ is used in industry for the manufacture of dyes. Thus, when cooled aniline is treated with HNO_2 it gives the diazonium base which on coupling with other molecules, such as phenol, gives bright coloured dyes:

$$C_6H_5NH_2 + HNO_2 \rightarrow C_6H_5N = NOH + H_2O$$

Hyponitrous acid, $H_2N_2O_2$

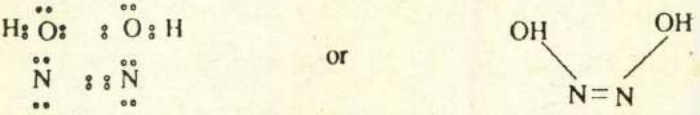
The salts of hyponitrous acid are generally made by reducing $NaNO_3$ or $NaNO_2$ with sodium amalgam (Na—Hg) giving $Na_2N_2O_2$. Ag-salt is precipitated from $Na_2N_2O_2$ by adding $AgNO_3$. Silver hyponitrite when reacted with HCl gas in ether gives $H_2N_2O_2$ in the ether solution. On evaporation the solution $H_2N_2O_2$ is obtained :

$$2\,NaNO_2 + 8H \xrightarrow{Na\text{-}Hg} Na_2N_2O_2 + 4H_2O$$

$$Na_2N_2O_2 + 2AgNO_3 \longrightarrow Ag_2N_2O_2 + 2NaNO_3$$

$$Ag_2N_2O_2 + 2HCl \xrightarrow{ether} 2AgCl + H_2N_2O_2$$

$K_2N_2O_2$ is also obtained by electrolysing KNO_2 solution. H_2 is evolved at the cathode which reduces KNO_2 to $K_2N_2O_2$. $H_2N_2O_2$ is a white crystalline solid having the formula :



All hyponitrites have also got the same structure :

$$NaO — N = N — ONa$$

$H_2N_2O_2$ gives a Pb-salt with Pb acetate and Ag-salt with $AgNO_3$. The Ag-salt, $Ag_2N_2O_2$, is soluble in acid but not in ammonia. $Na_2N_2O_2$ and also

$NaHN_2O_2$ are formed. The ethyl derivatives have also been prepared having the composition $(C_2H_5)_2N_2O_2$. The formula $H_2N_2O_2$ is supported from the vapour density measurements. The presence of azo group, —N = NO, is supported from the decomposition of $C_2H_5ON = NOC_2O_5$ which gives N_2 :

$$C_2H_5O—N = N—OC_2H_5 \rightarrow C_2H_5OH + CH_3CHO + N_2$$

PHOSPHORUS

Phosphorus is the second element of the nitrogen group. Although in many respects the chemistry of P resembles that of nitrogen as mentioned earlier and shows the gradation in properties, there are some marked contrasts as well.

Comparison between N and P

1. N_2 occurs in nature in the free state, P never occurs in the free state. In fact, phosphorus is the only element of the group V which does not occur in the free state.

2. The electronic structures of N and P are :

$$N—1s^2 2s^2 2p^3$$

$$P—1s^2 2s^2 2p^6 3s^2 3p^3$$

3. N_2 is an active gas whereas P is highly reactive in its white modification. The strength of P ≡ P bond is much less than N ≡ N bond.

4. N_2 is diatomic ; P is tetra-atomic (P_4) at ordinary condition.

5. Nitrogen combines with O_2 only at the high temperature in electric arc. Phosphorus burns in air on exposure liberating energy.

6. HNO_3 and HNO_2 are strong oxidizing agents whereas H_3PO_4 and H_3PO_3 are very weak oxidizing agents.

7. PH_3 is a greater reducing agent than NH_3.

8. Nitrogen forms double and triple bonds but such bonds in phosphorus are not common.

9. In aqueous solution N can exist as NH_4^+, NO_3^- and NO_2^- ions. Whereas P can exist as HPO_3^{-2}, PO_4^{-3} and such other ions.

10. Trivalent P is a greater reducing agent than trivalent N or trivalent As. This is a departure from the general gradation of properties in the Periodic Table.

Occurrence of P : Because it is very reactive with O_2, phosphorus does not occur free in nature. It occurs as :

Phosphorite—$Ca_3(PO_4)_2$

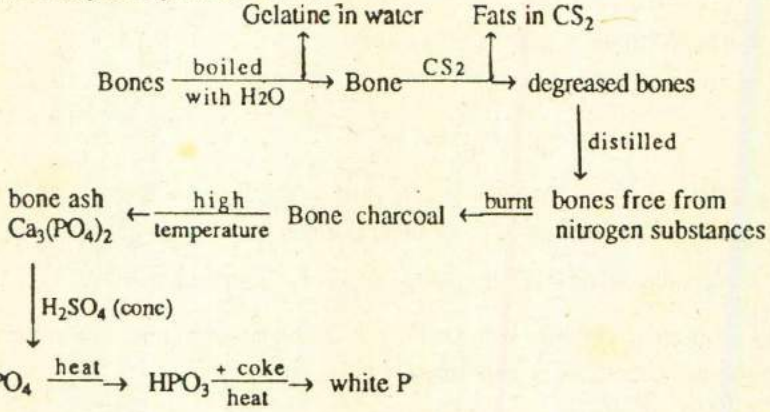
Fluorapatite—$Ca_{10}F_2(PO_4)_6$ or $3Ca_3(PO_4)_2.4CaF_2$

Chlorapatite—$Ca_{10}Cl_2(PO_4)_6$ or $3Ca_3(PO_4)_2.CaCl_2$

Phosphorus is essential to plants and animals ; bones, teeth and even muscle tissues contain P. Foods, such as eggs, beans, milk etc. provide P. Plants take up P from soil as soluble phosphates.

Preparation of phosphorus : White phosphorus is obtained from bone ash or a mineral phosphate. The flow sheet of the preparation is given below.

(a) Phosphorus from bone ash :



(b) Phosphorus from phosphate rock : Phosphorus is commercially obtained from phosphate rocks, $Ca_3(PO_4)_2$, by reduction with carbon in presence of silica (SiO_2) in an electric furnace heated by two stout carbon electrodes to temperatures of about 1500°C :

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C = 6CaSiO_3 + 10CO + P_4$$

The phosphorus is distilled off and condensed to the solid state or may be burnt into P_2O_5, i.e., P_4O_{10}, for the production of other compounds of P. The slag of $CaSiO_3$ along with CaF_2 or ferrophosphorus (formed from impurities in the ore or from apatite ore) is drawn off from the bottom of the furnace in the molten state. At the temperature of about 1150°C, P_2O_5 is formed which is converted to P_4 at about 1500°C :

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5$$

$$2P_2O_5 + 10\,C = P_4 + 10\,CO$$

The crude P is purified by melting under water and adding an oxidizing agent, such as $Na_2Cr_2O_7$, in presence of some acid and filtered through canvas bags. The pure P is cast into sticks and stored under water.

Properties of P : (1) The well-known white phosphorus is a wax-like thing, having low melting point of 44°C and it boils at 280°. It is volatile and readily soluble in CS_2.

(2) It is spontaneously inflammable in air and is poisonous. It is, therefore, stored and worked under water in which it is insoluble.

(3) The solid as well as the vapour consists of discrete molecule consisting of P_4 tetrahedra, each P shares a pair of electrons with each of the three other P. Each P has one lone pair of electrons as shown in Fig. 20—2.

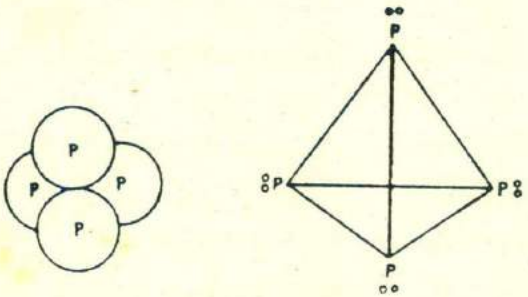


Fig. 20—2. P_4 molecule.

(4) Phosphorus gives green glow in the dark, the phenomenon is known as *phosphorescence*.

(5) In the vapour state at very high temperature P consists of P_2 molecules similar to N_2 i.e. (: P : : : P :).

(6) White P is converted to red P, another allotropic from, by heating to 230—400°C in iron retorts in absence of air. The change is catalysed by a trace of iodine :

$$P\ (white) \rightleftharpoons P\ (red) + 4\ Kcal$$

White P changes to red P slowly on exposure to light. Red phosphorus consists of aggregates and, because heat is liberated during the change from white P to red P, the heat of combustion of red P is less than that of white P. It does not inflame in air at ordinary temperature and is insoluble in CS_2. It is much less reactive and not poisonous. Its melting point is 593°C. A black variety of P is also formed which is electrically conductive having lamellar structure like graphite.

Reactions of Phosphorus

(a) Reaction with oxygen : P has ignition temperature of only 35—45°C and hence it burns spontaneously due to the initial slow reaction of P with atmospheric oxygen at room temperature. Depending upon the supply of oxygen. P_4O_{10} and P_4O_6 may be formed :

$$P_4 + 5O_2 \longrightarrow P_4O_{10}\ (\text{ample supply of } O_2)$$

$$P_4 + 3O_2 \longrightarrow P_4O_6\ (\text{limited supply of } O_2)$$

(b) Reactions with H_2 : P does not react with H_2 in the elementary state. hydrides of P are obtained by reaction with alkali.

(c) Reaction with halogens : P reacts directly with all halogens forming PX_3. The reactions with F_2 is very vigorous :

$$P_4 + 6F_2 \rightarrow 4PF_3\ (\text{colourless gas})$$

$$P_4 + 6Cl_2 \rightarrow 4PCl_3\ (\text{colourless liquid}))$$

$$P_4 + 6Br_2 \rightarrow 4PBr_3\ (\text{colourless liquid}))$$

$$P_4 + 6I_2 \rightarrow 4PI_3\ (\text{orange solid})$$

(d) Reactions with metals : Alkali and alkaline earth metals react with P on heating forming phosphides like nitrides, e. g., Na_3P, Ca_3P_2 etc.

(e) Reactions with HNO₃ : P is oxidized to H_3PO_4 by conc HNO_3 :

$$P + 5HNO_3 = H_3PO_4 + 5NO_2 + H_2O$$

(f) Reaction with alkali : P reacts with NaOH to give PH_3 :

$$4P + 2H_2O + 3NaOH = PH_3 + 3NaH_2PO_2$$

(g) Reactions with S : With S it combines on heating to form P_4S_3, P_4S_7 and P_4S_{10} depending on the ratios of the components used and the reaction conditions.

Red phosphorus : By heating white P alone or in light or in presence of a catalyst, such as iodine, it produces the allotropic modification of phosphorus.

Properties of red P : (1) Red P is non-poisonous. (2) It is insoluble in CS_2. (3) Chemically it is less reactive than white phosphorus.

Uses of Phosphorus

Phosphorus is used in,

(1) Manufacture of matches.

(2) Production of acids of phosphorus and their salts for fertilizers.

(3) Special alloys, such as phosphor bronze.

(4) In incendiary bombs and explosives.

Match Industry : Formerly white phosphorus was used in the manufacture of matches, but workers in the factory suffered from *Phossy jaw* or necrosis of the bones. It has now been replaced by phosphorus sulphide, P_4S_3, and also in safety match by antimony trisulphide, Sb_2S_3.

Three types of matches have been developed : (1) Lucifer matches, (2) safety friction matches and (3) safety matches.

Lucifer matches and friction matches consists of P_4S_3 at the tip of the match-head together with $KClO_3$, sulphur, sand and binding material (glue). The

stick is impregnated with ammonium phosphate and paraffin. These matches can be lighted by striking anywhere on a rough surface.

The heads of the safety matches contain no phosphorus but Sb_2S_3 mixed with an oxidizing agent, such as $K_2Cr_2O_7$ or red lead and fixed with glue. The surface on the side of the box consists of red phosphorus and powdered glass mixed with glue. The head of the safety match can be lighted only on rubbing against this special surface on the side of the match box. It is not ignited by friction anywhere else. The glass powder or sand is added to reduce sensitivity of the matches and to provide friction.

The match sticks are given initial coat of sulphur or paraffin to help combustion. Impregnation in borax or ammonium phosphate solution prevents the flame from glowing after it has been extinguished.

The match industry is now a highly mechanized process. The splints are produced in machines from logs of wood and also the flat thin sheets of wood which are made into boxes. The process of match industry is highly automatic. From the start to the finish the packing is done by automation.

Compounds of Phosphorus

1. Hydrides of phosphorus : P forms a series of hydrides, the most important of which is *phosphine*, PH_3. Others are P_2H_4, $P_{12}H_6$, P_5H_2, P_9H_2. Phosphine is a gas, P_2H_4 is liquid and all others are solid.

PH_3 is prepared by heating white phosphorus in a concentrated solution of NaOH. Phosphine prepared in this way is spontaneously inflammable forming a fog of phosphoric acid when bubbled through water. The fog rise in the air in the form of smoke rings :

$$P_4 + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3$$

It has been found that pure PH_3 is not inflammable, but prepared by the above method, it contains some P_2H_4 which ignites with PH_3.

PH_3 is also formed by the reactions :

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

$$AlP + 5H_2O \xrightarrow{\text{acid}} Al(OH)_3 + PH_3$$

The reaction of O_2 (air) on PH_3 is given by the equation :

$$PH_3 + 2\,O_2 = H_3PO_4$$

Non-inflammable PH_3 is obtained when P is heated with alcoholic solution of KOH or when Ca_3P_2 is reacted with HCl.

PH_3 is a much weaker base than NH_3 because it shows less tendency to donate a pair of electrons to a H^+ ion. PH_3 is decomposed on heating to P_4 and H_2. PH_3 combines with HCl, HBr or HI to form *phosphonium compounds*, PH_4Cl, PH_4Br and PH_4I. In aqueous solutions PH_4^+, ions are unstable, easily hydrolysed and give off PH_3. PH_4^+ ion is essentially a strong acid :

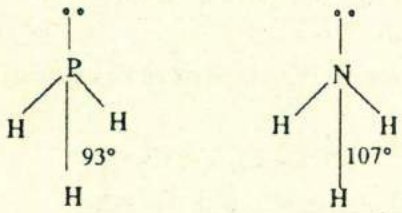
$$PH_4I + H_2O = PH_3 + HI + H_2O$$

PH_4I is best obtained by the reaction of white P with iodine in CS_2 solution to which water is added while heating :

$$9P + 5I + 16H_2O = 5PH_4I + 4H_3PO_4$$

Like NH_3, phosphine forms coordination compounds, e. g. $Cl_3B{:}PH_3$.

PH_3 has the same structure as NH_3 using sp^3 bonds of P in the tetrahedral positions with a lone pair of electrons at one corner. But P—H bonds are much larger than N—H and also H—P—H angle is smaller than H—N—H angle :



Phosphorus halides : P forms the halides of general formula PX_3 and PX_5 with all the halogens. PI_5 is not known. These are much more stable than the corresponding compounds of nitrogen. Here only PCl_3 and PCl_5 are described.

Phosphorus trichloride, PCl_3, is prepared by passing dry Cl_2 over molten phosphorus :

$$P_4 + 6Cl_2 = 4PCl_3$$

It can also be prepared by the action of thionyl chloride on P :

$$2P + 4SOCl_2 = PCl_3 + 2SO_2 + S_2Cl_2$$

PCl_3 is a colourless liquid and is completely hydrolysed by water to give H_3PO_3 and HCl, and even in moist air:

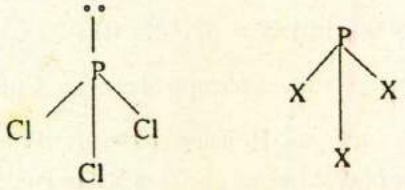
$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

Generally, the phosphorus trihalides are rapidly attacked by water:

$$PX_3 + 3H_2O \rightarrow H_3PO_3 + 3\,HX$$

These reaction are used for the preparation of HBr and HI.

PCl_3 has the pyramidal structure given below in which P uses the sp^3 orbitals to form the bonds with 3Cl :



The bonds may also be described as due to the sp^3 bonds of P as in PH_3 and NH_3. PCl_3 can replace CO in $Ni(CO)_4$ forming $Ni(PCl_3)_4$ showing the coordinating action of PCl_3.

Phosphorus pentachloride, PCl_5, is prepared by oxidizing PCl_3 with excess of Cl_2 :

$$PCl_3 + Cl_2 = PCl_5$$

Sulphuryl chloride also gives PCl_5 with P or PCl_3 :

$$P_4 + 10SO_2Cl_2 = 4PCl_5 + 10SO_2$$

$$PCl_3 + SO_2Cl_2 = PCl_5 + SO_2$$

PCl_5 is a straw-coloured solid and dissociates reversibly and sublimes :

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

PCl_5 is hydrolysed as :

$$PCl_5 + H_2O = POCl_3 + 2HCl$$

Excess H_2O gives :

$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl$$

In the vapour and liquid state PCl_5 has a trigonal bipyramidal structure as given in Fig. 20—3.

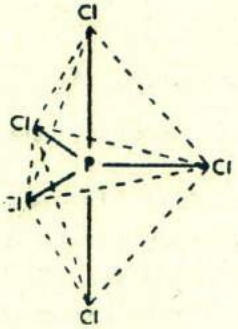


Fig. 20—3. PCl_5 molecule.

The reason why PCl_5 is formed and not NCl_5 is that N atom having the electronic structure $1s^2\ 2s^2\ 2p^3$ has no stable d orbitals available to form 5. bonds by using $3s^1\ 3p_x^1\ 3p_y^1\ 3p_z^1\ 3d^1$ or $3s^1\ 3p^3\ 3d^1$ (sp^3d) hybrid bonding orbitals.

In the solid state PCl_5 consists of an ionic structure $[PCl_4]^+[PCl_6]^-$. The cation $[PCl_4]^+$ has the tetrahedral structure and the anion $[PCl_6]^-$ has octahedral structure.

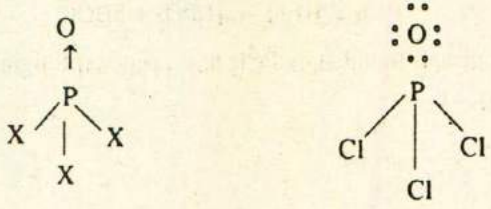
Phosphorus oxyhalides, POX_3, are readily obtained by the action of PCl_5 on P_2O_5, i.e., P_4O_{10}:

$$6PX_5 + P_4O_{10} = 10POX_3$$

Partial hydrolysis of PCl_5 gives $POCl_3$ as mentioned before.POX_3 is completely hydrolysed in water :

$$POX_3 + 3H_2O = H_3PO_4 + 3HX$$

The structure is tetrahedral as shown below :



Oxides of Phosphorus

P forms several oxides of which P_4O_6, P_8O_{16} and P_4O_{10} are well-defined.

The combustion of P in air generally produces a mixture of P_4O_6 and P_4O_{10}.

Phosphorus(III)oxides, P_4O_6 : This compound is often called phosphorus trioxide. It is a white crystalline solid having melting point of 22.5°C. On heating, it is decomposed to red P and P_8O_{16}. P_4O_6 is made by burning white P in a limited supply of air. With cold water P_4O_6 gives H_3PO_3 but with hot water it gives H_3PO_4 and PH_3 :

$$P_4 + 3O_2 \rightarrow P_4O_6$$

$$P_4 + 6H_2O \rightarrow 4H_3PO_3$$

$$4H_3PO_3 \xrightarrow{\text{heat}} 3H_3PO_4 + PH_3$$

Phosphorus(V)oxide, P_4O_{10} : It is commonly called phosphorus pentoxide and is represented as P_2O_5. It is obtained by burning P in excess of air or oxygen. It is a white flocculent powder and melts at 800°C. It is quite stable. With water it forms H_3PO_4 and also HPO_3 (in limited amount of water) :

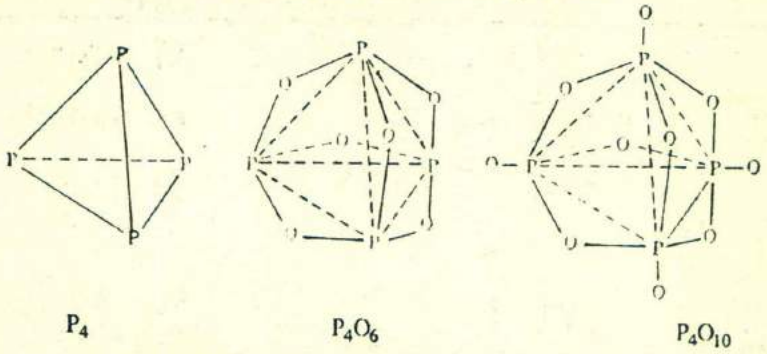
$$P_4O_{10} + 2H_2O = 4HPO_3$$

$$P_4O_{10} + 6H_2O = 4H_3PO_4$$

P_4O_{10} is used as an efficient drying agent and also for removing water from many hydroxy compounds.

The structure of P_4O_6 and P_4O_{10} are related to P_4 molecules. P_4 tetrahedra has six P—P bonds. In P_4O_6, each of P—P bonds is changed to P—O—P

bridge. If an extra O atom is attached to each P in P_4O_6, it gives P_4O_{10}. Sketches of these structural changes are shown in Fig. 20—4.



P_4 P_4O_6 P_4O_{10}

Fig. 20—4. Structures of P_4O_6 and P_4O_{10} in relation to P_4

Oxyacids of Phosphorus

Phosphorus froms a number of oxyacids and these can be classified in two groups :

1. Oxyacids of phosphorus (V).

2. Oxyacids of phosphorus (III).

1. The oxyacids of P(V) : The well-known oxyacids of +5 state of P are :

H_3PO_4 — Orthophosphoric acid.

$H_4P_2O_7$ — Pyrophosphoric acid.

$(HPO_3)n$ —Metraphosphoric acid.

The structural formula and the number of OH groups in the acids (basicity of the acids) of P(V) acids are given in Table 20.4.

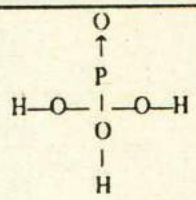
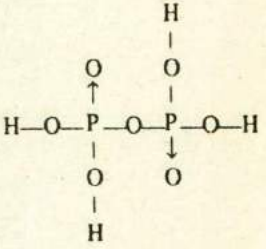
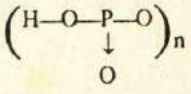
2. The oxyacids of P(III) : The oxyacids of P in +3 oxidation states are :

H_3PO_3—Orthophosphorous acid.

$H_4P_2O_5$—Pyrophosphorous acid.

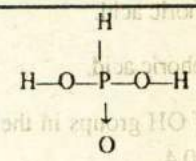
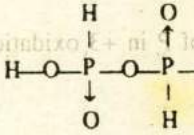
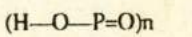
$(HPO_2)_n$—Metaphosphorous acid.

Table 20.4. Oxyacids of P(V)(P^{+5}).

Formula	*Structural formula*	*No. of OH groups*	*Ionization constants at 20°C*
H_3PO_4 Ortho–		3	$K_1 = 7.5\times10^{-3}$ $K_2 = 6{\cdot}2\times10^{-8}$ $K_3 = 1\times10^{-13}$
$H_4P_2O_7$ Pyro–		4	$K_1 = 1.4\times10^{-1}$ $K_2 = 1{\cdot}1\times10^{-2}$ $K_3 = 2{\cdot}1\times10^{-7}$ $K_4 = 4{\cdot}0\times10^{-10}$
$(HPO_3)_n$ Meta—		n n = 6 or more	—

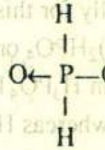
The structural formula and the number of OH groups in acids of P (III) are given in Table 20.5.

Table 20.5. Oxyacids of phosphorus(III) (P^{+3}).

Formula	*Structural formula*	*No. of OH groups*	*Ionization constants in aq. soln. at 20°C*
H_3PO_3 Ortho-		2	$K_1 = 2\times10^{-2}$ $K_2 = 2\times10^{-7}$
$H_4P_2O_5$		2	—
$(HPO_2)_n$		n n = 6 or more	—

Besides the above two groups of oxyacids of phosphorus we can also include the following :

H_3PO_2—Hypophosphorous acid.



H_3PO_5—Permonophosphoric acid

$H_4P_2O_8$—Perdiphosphoric Acid.

Orthophosphoric acid, H_3PO_4 : This is also known as phosphoric acid and is obtained by various processes.

1. When P_4O_{10} is fully dissolved in water H_3PO_4 is produced :

2. PCl_5 on complete hydrolysis gives H_3PO_4 :

$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl$$

3. Oxidation of P with HNO_3 :

$$P_4 + 20\ HNO_3 = 4H_3PO_4 + 4H_2O + 20\ NO_2$$

4. H_3PO_4 is manufactured from $Ca_3(PO_4)_2$ by heating with H_2SO_4 :

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 2H_3PO_4 + 3CaSO_4$$

Properties : H_3PO_4 has three replaceable H atoms because each H is covalently bonded to O atom which is in turn bonded to P. The ionization constants K_1, K_2, K_3 of H_3PO_4 indicate that there is only one strong H^+ ion, the other two have decreased acid or ionization character:

$$H_3PO_4 \overset{K_1}{\rightleftharpoons} H^+ + H_2PO_4^- \overset{K_2}{\rightleftharpoons} H^+ + HPO_4^{-2} \overset{K_3}{\rightleftharpoons} H^+ + PO_4^{-3}$$

Since PO_4^{-3} concentrations in H_3PO_4 solutions are exceedingly small phosphates containing PO_4^{-3} ion are normally not precipitated from H_3PO_4 solutions. Generally for this purpose, compounds containing $H_2PO_4^-$ or HPO_4^{-2} ions such as $(NH_4)_2HPO_4$ or NaH_2PO_4 are used. Moreover, H_2SO_4 and HNO_3 are stronger acids than H_3PO_4 because H_2SO_4 and HNO_3 are fully dissociated into ions in solutions whereas H_3PO_4 is not.

H_3PO_4 thus forms three series of salts containing $H_2PO_4^-$, HPO_4^{-2} and PO_4^{-3} ions which are known as primary, secondary and tertiary phosphates. It is evident that in dilute solutions the soluble phosphates give acidic, less acidic and basic reactions depending on the anionic species. Thus NaH_2PO_4 gives acidic reaction. Na_2HPO_4 slightly basic but Na_3PO_4 gives alkaline solutions :

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{-2} + H_3O^+$$

$$HPO_4^{-2} + H_2O \rightleftharpoons PO_4^{-3} + H_3O^+$$

$$PO_4^{-3} + H_2O \rightleftharpoons HPO_4^{-2} + OH^-$$

In concentrated solution and at high temperatures the reactions of H_3PO_4 become complicated by means of condensation reaction. The PO_4 groups having the tetrahedral structure are linked together by sharing oxygen atoms forming in the long run polyphosphate. This phenomenon of polymerisation is particularly important when phosphates are heated to higher temperatures.

It is to be noted that when the ortho-phosphates, particularly the primary and the secondary phosphates are heated, the products obtained may be meta-, pyro- or poly-phosphates :

$$2H_3PO_4 \xrightarrow[\text{heat}]{\text{low}} H_4P_2O_7 \xrightarrow{200°C} 2HPO_3 + H_2O$$

$$2Na_2HPO_4 \xrightarrow{\text{heat}} Na_4P_2O_7 + H_2O$$

Calcium superphosphate : Calcium forms three salts with phosphates, $Ca(H_2PO_4)_2$, $CaHPO_4$ and $Ca_3(PO_4)_2$. The hydrogen phosphates are soluble to some extent and are used as fertilizers for plants. This compound, $Ca(H_2PO_4)_2$, is prepared commercially by treating $Ca_3(PO_4)_2$ with H_2SO_4 :

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O = Ca(H_2PO_4)_2 + 2CaSO_4.2H_2O$$

The mixture of $Ca(H_2PO_4)_2$ and $CaSO_4.2H_2O$ is called *super-phosphate of lime or calcium superphosphate. TSP or Triple superphosphate of lime* is a product containing higher percentage of phosphate. This is manufactured by treating pulverized calcium phosphate, $Ca_3(PO_4)_2$, with H_3PO_4 :

$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3Ca(H_2PO_4)_2$$

Large quantities of superphosphates are produced for use as fertilizers under the controlled conditions of concentration of H_3PO_4, quantity of water, proper mixing and formation of the granular products. *MSP* (monosuperphosphate) is also produced.

Pyrophosphoric acid, $H_4P_2O_7$: This is prepared by heating H_3PO_4 to 250°C :

$$2H_3PO_4 \rightleftharpoons H_4P_2O_7 + H_2O$$

The reaction of H_3PO_4 and HPO_3 at 100°C also gives $H_4P_2O_7$:

$$H_3PO_4 + HPO_3 = H_4P_2O_7$$

Pyrophosphoric acid is a white solid which melts at 61°C. It is gradually hydrolysed to ortho acid in water. The normal pyrophosphates are prepared by heating dihydrogen phosphate :

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O$$

$$2CaHPO_4 = Ca_2P_2O_7 + H_2O$$

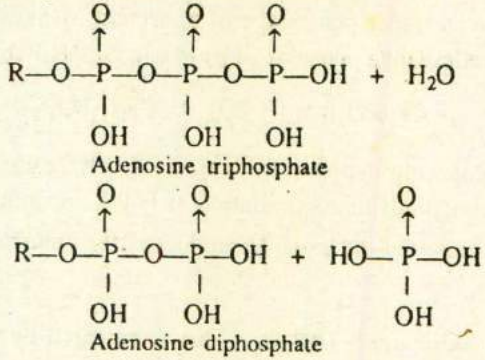
The well-known case of $MgNH_4PO_4$ or $ZnNH_4PO_4$ formerly used in quantitative analysis by ignition to $Mg_2P_2O_7$ or $Zn_2P_2O_7$ depends on the reaction :

$$2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O$$

Triphosphoric acid, $H_5P_3O_{10}$, is formed by elimination of two molecules of H_2O from three molecules of H_3PO_4.

Polyphosphate linkages have great biochemical importance. The energetic hydrolysis of a complex organic ploy phosphate known as adenosine triphosphate in muscle tissues provides 10 Kcal of energy per mole of adenosine triphosphate.

Representing the complex organic part of the molecules as R—, the following equation may be written for the reaction :



Metaphosphoric acid, $(HPO_3)_n$: This is also obtained by a number of methods as given by the equations :

$$(a)\ P_4O_{10} + 2H_2O = 4HPO_3$$

$$(b)\ H_3PO_4 \xrightarrow[400°C]{-H_2O} HPO_3 + H_2O$$

$$(c)\ Pb(PO_3)_2 + H_2S = PbS + 2HPO_3$$

Metaphosphoric acid forms transparent glassy product, called *glacial phosphoric acid*. The P—O—P linkages in $(HPO_3)_n$ form rings and chains. HPO_3 molecules polymerise to give $(HPO_3)_n$. The acid is slowly hydrolysed to give H_3PO_4. The salts of HPO_3, i.e., metaphosphates are obtained by heating dihydrogen phosphate, e.g., NaH_2PO_4 :

$$nNaH_2PO_4 = (NaPO_3)_n + nH_2O$$

If the product is heated to 700°C and then rapidly cooled a glassy *Polymetaphosphate* is obtained. This is generally known as *Graham's salt* and has ben given the formula $(NaPO_3)_6$ or *Sodium hexametaphophate*. This is not the correct composition but it is rather more complex and contains a number of different polyphosphate ions. This is also obtained by heating microcosmic salt, $NaHNH_4PO_4.4H_2O$. If the heated product is cooled slowly it gives $(NaPO_3)_3$.

Sodium hexametaphophate is soluble in water and forms soluble complexes with Ca^{+2} even when Ca is present as $CaCO_3$, CaC_2O_4, $CaSO_4$ etc. This is,

therefore, used for removing scales from the boilers and softening of hard water and as detergents. The detergent action is due to (i) complexation of Ca ion and softening of water : (ii) formation of highly charged ions which attract particles of dirt. The resultant dirt particles repel one another and are rinsed off with water.

The distinctive tests for ortho-, meta- and pyro-phosphoric acids or their salts in solutions are given below :

	Reagent	*Ortho-* H_3PO_4	*Meta-* HPO_3	*Pyro-* $H_4P_2O_7$
1.	$AgNO_3$	Orange-yellow ppt.	White ppt.	White ppt.
2.	Albumin	No change	Coagulated	No change
3.	Ammonium molybdate	Yellow ppt.	×	×

In order to test for PO_4^{-3} ions all phosphorus compounds must be converted to the PO_4^{-3} form by oxidation with HNO_3. It is H_3PO_4 which gives the yellow precipitate of ammonium phospho-molybdate with ammonium molybdate. This is a sensitive test for phosphorus :

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21\ HNO_3 \rightarrow (NH_4)_3PO_4.12MoO_3$$
$$+21\ NH_4NO_3 + 12H_2O$$
$$\text{or } (NH_4)_3[PMo_{12}O_{40}]$$

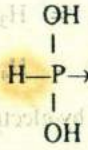
Phosphorous acid, H_3PO_3 : This can be made by hydrolysing P_4O_6, PCl_3, PBr_3 or PI_3 :

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

H_3PO_3 is a white crystalline substance, deliquescent and highly soluble in water with a garlic odour. It melts at 70°C. Its decomposition at 200°C is an example of auto-oxidation-reduction reaction giving PH_3 and H_3PO_4 :

$$4H_3PO_3 = PH_3 + 3H_3PO_4$$

H_3PO_3 has only two ionizable H indicating one H to be covalently bonded with P :



H_3PO_3 and its salts phosphites are active reducing agents because these are easily oxidized to H_3PO_4 and phosphates respectively. Thus it reduces silver salts to Ag, mercury salts to mercurous salts and SO_2 to sulphur.

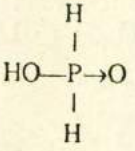
Two series of salts are obtained having the compositions, as in NaH_2PO_3 and Na_2HPO_3. When NaH_2PO_3 is heated Na-salt of pyrophosphorous acid is formed. Metaphophites are also polymers like metaphosphates.

Hypophosphorous acid, H_3PO_2 : The solution which is left after the preparation of PH_3 by the reaction of white P and NaOH, contains NaH_2PO_2. H_3PO_2 may be obtained by the following reactions in which NaOH is replaced by $Ba(OH)_2$ for the preparation of PH_3 :

$$3Ba(OH)_2 + 2P_4 + 6H_2O = 3Ba(H_2PO_2)_2 + 2PH_3$$

Barium hypophosphite on treatment with H_2SO_4 gives free H_3PO_2 :

The filtrate on evaporation gives a syrupy liquid. It is a mono-basic acid having only one ionizable H^+ ion. The other two H are covalently linked to P :



H_3PO_2 gives only one series of salts known as hypophosphites.

These are soluble in water and alcohol and possess reducing properties because P^{+1} is readily changed to P^{+3} state :

$$H_3PO_2 + Cl_2 + H_2O = H_3PO_3 + 2HCl$$

$$H_3PO_2 + Fe^{+3} + 3H_2O = H_3PO_3 + 2Fe^{+2} + 2H_2O$$

Perphosphoric acid : H_3PO_5 is obtained on adding H_2O_2 to P_4O_{10} at low temperature. $H_4P_2O_7$ on treatment with H_2O_2 gives $H_4P_2O_8$:

$$H_3PO_4 + H_2O_2 = H_3PO_5 + H_2O$$

$$H_4P_2O_7 + H_2O_2 = H_4P_2O_8 + H_2O$$

The salts of these acids are produced by electrolytic methods.

Some Compounds of As, Sb and Bi

The compounds of N, P, As, Sb and Bi differ in their stability in some cases and there is some departure from the regular gradation of properties as well. For instance, PCl_5 is more stable than $AsCl_5$. Some of the compounds of As, Sb and Bi in their different oxidation states are given in Table 20.6 These give some idea as regards the stability of the various oxidation states of the elements.

Table 20.6. Compounds of As, Sb and Bi.

Oxidation states	*As*	*Sb*	*Bi*
−3	AsH_3	SbH_3	BiH_3
+3	As_4O_6	Sb_4O_6	Bi_4O_6
	As_4S_6	Sb_2S_3	Bi_2S_3
	H_3AsO_3	H_3SbO_3	—
	$NaAsO_2$	$NaSbO_2$	—
	$AsCl_3$	$SbCl_3$	$BiCl_3$
+5	As_4O_{10}	Sb_4O_{10}	—
	H_3AsO_4	H_3SbO_4	$HBiO_3$
	Na_3AsO_4	Na_3SbO_4	$NaBiO_3$
	—	$SbCl_5$	—

As, Sb and Bi form a large number of organo-compounds in conformity with the properties of N and P which are essential for organic substances as mentioned before.

Potassium antimonyl tartrate, $KSbOC_4H_4O_6$, is formed when potassium hydrogen tartrate and Sb_2O_3 are heated together. The product is known as *tartar emetic*. The compound contains SbO^+ ion. It is used as a medicine.

Potassium pyroantimonate, $K[Sb(OH)_6]$, $0.5H_2O$ or $K_2H_2Sb_2O_7$, $5H_2O$: This is soluble in water and is used as a reagent for Na^+ ion. The Na-salt of pyroantimonate, $Na[Sb(OH)_6]$ is insoluble in water and hence on addition of potassium pyroantimonate solution, in the hot condition, the sodium compound is formed as a white precipitate.

Sodium bismuthate, $NaBiO_3$: It is brown powder and the composition is uncertain. However, it is an oxidizing agent used in analytical chemistry and the

composition is $NaBiO_3$. It is particularly used for the determination of manganese in steel. Mn^{+2} in HNO_3 is oxidized to MnO_4^- by $NaBiO_3$:

$$2Mn^{+2} + 5\ NaBiO_3 + 14H^+ \rightarrow 2MnO_4^- + 5Bi^{+3} + 5\ Na^+ + 7H_2O$$

Antimony and Bismuth oxyhalides SbOX and BiOX: When excess of water is added to a solution containing Sb or Bi in, say HCl, SbOCl and BiOCl are precipitated out from their respective solutions. SbOCl is white crystalline substance. It is very slowly hydrolysed by water. It is insoluble in alcohol and ether but soluble in CS_2, C_6H_6 and $CHCl_3$ indicating covalent antimonyl chloride, SbOCl. Other halides and nitrate and sulphate of antimony behave similarly :

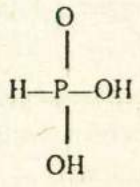
$$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$$

BiOCl is more stable than SbOCl and is not hydrolysed by water or alkali.

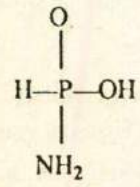
Water in large quantity is, therefore, used as a reagent for Sb or Bi, the presence of which is indicated by the formation of white precipitate.

N-P compounds

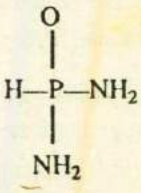
A number of compounds have been reported which contain N—P bond together :



Phosphorous acid



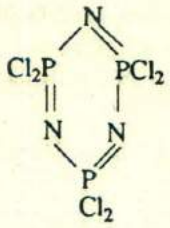
Amidophosphorous acid



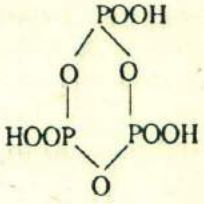
Diamido phosphorous acid

Cyclic Compounds of P : A series of phosphonitrilic halides (phosphazines) having the general formula $(PNX_2)n$ have ben prepared. These are polymers and the most important is the trimer, $P_3N_3Cl_6$, having benzene-like ring. In fact, this resembles the trimetaphosphate :

These are rubber-like substances (inorganic rubbers) but they are hydrolysed in water to give Cl^-, NH_4^+ and H_3PO_4.



Phosphazine



Trimetaphophoric acid

The Vanadium Group Metals

The properties of these transition metals are listed in Table 20·2(b) page 496 and comparisons of some of their compounds throw some light on their chemistry. Because these metals are transition metals, they have variable oxidation states due to five valence electrons. Oxidation states of +5 is the characteristic of V, Nb and Ta. For Nb and Ta it is the only important oxidation state as in Nb_2O_5 and Ta_2O_5. The difference of electron arrangements in $Nb(4d^45s^1)$ and $Ta(5d^36s^2)$ does not affect their chemical behaviour. The respective sizes of their ions are almost similar which make their chemical behaviour almost identical like those of Hf and Zr. Vanadium show variable oxidation states.

Vanadium group metals are hard and have very high melting points. They show passivity towards acids, particularly Ta. The compounds of V, Nb and Ta are all obtained from their respective oxides V_2O_5, Nb_2O_5, Ta_2O_5.

QUESTIONS AND PROBLEMS

1. Give the preparation, properties and uses of oxides and oxyacids of phosphorus.
2. Give a comparative study of the chemistry of nitrogen and phosphorus and that of their compounds.
3. Starting with phosphorus how will you obtain phosphoric acid ?
   How is phosphate detected in a solution ?
4. Describe the preparation, properties and structure of :—(a) Nitrous oxide and (b) phosphorus pentoxide.

5. Describe the methods for the synthesis of ammonia explaining clearly the physico-chemical principles on which it is based. Explain what happens when a solution of ammonia is added to —(a) silver chloride, (b) a solution of $HgCl_2$, (c) an alkaline solution of KI.
6. Write an account of the oxyacids of phosphorus. Discuss their properties and constitution.
7. Write a note on the natural and artificial fixation of nitrogen.
8. Describe the various methods used for the industrial preparation of nitric acid.
9. Give an account of the chemistry of match industry.
10. How is nitric acid prepared industrially ? What is the action of nitric acid on copper, tin and zinc ?
11. How is orthophosphoric acid prepared from—(i) bone ash, (ii) phosphorus ? How is orthophosphoric acid converted into other phosphoric acids.
12. Write a note on the match industry.
13. Write an eassay on the fixation of atmospheric nitrogen.
14. Write notes on—(i) Chloride of phosphorus. (ii) Nitrogen tetroxide.
15. How would you prepare orthophosphoric acid from phosphate rock?
16. Write a brief note on action of ammonia on salts of mercury and silver?
17. Name the inorganic compounds containing nitrogen and phosphorus used as fertilizers. Discuss in detail the manufacture of any two of them.
18. Write a detailed account on the oxide of nitrogen with special reference to their preparation, properties and structure.
19. Discuss the uses of—(i) microcosmic salt, (ii) sodium cobaltinitrite, (iii) stannous chloride, (iv) Nessler's reagent in analytical chemistry.
20. Describe the preparation and properties of the following :—(i) nitrosyl chloride, (ii) nitrososulphuric acid, (iii) dinitrogen trioxide.
21. Write an analytical scheme for the detection and separation of arsenic, antimony and tin in a mixture. Give important chemical equations.
22. Compare the chemistry of nitrogen and phosphorus, including their oxides and oxyacids.
23. Compare the chemistry of nitrogen and phosphorus.
24. Write a note on oxides and oxyacids of phosphorus.
25. "Nitrogen is an inactive gas". Discuss.
26. Discuss the bonding systems and the shapes of NH_3 and PCl_5.
27. Which of the oxides of nitrogen are designated as odd molecules. Write their structures.

28. Ammonia is a Lewis base. What happens when it reacts with H_3O^+ ion in HCl solution ?
29. Ammonia and hydrazine have some similar properties. Discuss.
30. Why white phosphorus is stored under water ?
31. Why PCl_5 is formed but no NCl_5 occur ?
32. Phosphine is less stable and less basic then ammonia. Explain.
33. What is TSP ? How it is made ? For what purpose TSP is used ?
34. The formula for nitric acid is HNO_3 whereas that of phosphoric acid is H_3PO_4. Why ?

CHAPTER 21

OXYGEN, SULPHUR AND CHROMIUM

(The Elements of Group VI)

The elements of group VI are sub-divided into two sub-groups—VIA and VIB.

Group VIA	*Group VIB*
O — Oxygen	
S — Sulphur	
Se — Selenium	Cr — Chromium
Te — Tellurium	Mo — Molybdenum
Po — Polonium	W — Tungsten

THE OXYGEN OR SULPHUR FAMILY

(The Chalcogens)

The elements of group VIA consisting of O, S, Se, Te and Po are sometimes called chalcogens (which means chalk-formers) as is the nomenclature in the case of halogens (meaning salt-formers). Oxygen, the first member of group VIA, differs from the rest of the elements and hence the name *Sulphur Family* is more appropriate. In this book, we shall mainly deal with some aspects of chemistry of oxygen and sulphur and that of chromium from sub-group VIB. The general chemistry and their relationships with each other is restricted to some salient features. The element polonium is radioactive element.

Table 21.1. Electronic structures of Sulphur Family.

At. No.	*Elements*	*Electronic structure*	*Valence electrons*
8	O	He core, $2s^2 2p^4$	$2s^2\ 2p^4$
16	S	Ne core, $3s^2 3p^4$	$3s^2\ 3p^4$
34	Se	Ar core, $3d^{10} 4s^2 4p^4$	$4s^2\ 4p^4$
52	Te	Kr core, $4d^{10} 5s^2 5p^4$	$5s^2\ 5p^4$
84	Po	Xe core, $4f^{14} 5d^{10} 6s^2 6p^4$	$6s^2\ 6p^4$

The electronic structures of the group VIA are given in Table 21.1

The six electrons in the outermost energy levels are s^2p^4 electrons in each of the elements. The group VIB elements are transition metals and will be discussed at the end of this chapter separately.

Before discussing the chemistry of the elements on the basis of s^2p^4 electrons, a list of physical properties are given in Table 21.2

Table 21.2. Physical properties of the Sulphur Family.

Physical properties	*O*	*S*	*Se*	*Te*
Atomic No.	8	16	34	52
Atomic weight	16.00	32.006	78.96	127.61
Physical state	colourless gas	yellow solid	red or grey solid	silvery solid
Outer electron orbitals	$2s^22p_x^2$ $2p_y^12p_z^1$	$3s^23p_x^2$ $3p_y^13p_z^1$	$4s^24p_x^2$ $4p_y^14p_z^1$	$5s^25p_x^2$ $5p_y^15p_z^1$
Atomic or covalent radius (Å)	1.32	1.74	1.91	2.03
Ionic radius X^{-2} ion (Å)	0.47	1.06	1.16	1.44
Ionization energy (ev)	13.60	10.40	9.80	9.00
Melting point (°C)	−219	119	220	450
Boiling point (°C)	−183	415	688	1390
Electronegativity	3.50	2.50	2.40	2.10
Oxidation potential X^{-2}/X (v)	−1.23	+0.51	+0.77	+0.91
Oxidation states	+2, 0,−2, −1	−2, 0, +2, +4, +6	−2, 0,+4, +6	−2, 0, +2 +6

Comparison of Oxygen with Sulphur Group : Oxygen differs from the rest of the Sulphur Family in many respects. for instance :

(1) Oxygen is a colourless gas, others are all solids with S as non-metal, and the metallic character increase with the increasing atomic number.

(2) The six valence electrons in these elements consist of s^2p^4 arrangement.

(3) Oxygen occurs abundantly in nature in the free state and both in the inorganic and organic materials.

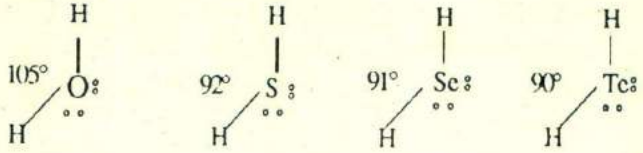
(4) Oxygen adopts generally the negative oxidation state of –2 much more readily as compared to other elements. The 6 electrons in the outermost level take up 2 electrons to form X^{-2} ion in this group. But this tendency decreases in the order O > S > Se > Te > Po. Oxygen in –2 state is present in all combined materials. The tendency to form negative oxidation states is less in other elements of this group. Hence O_2 is the strongest oxidizing agent and Te the weakest. Oxygen does not lose 6 electrons to assume +6 state which is quite common for S, Se and Te.

(5) Oxygen having small atomic volume and high ionization potential as compared to the other elements of the group is characterised with the difference in physical constants which result in special properties of oxygen.

(6) Oxygen is more electronegative than any other element except fluorine. This is one reason for the special properties of oxygen in its compounds. For instance, all the elements of this group form hydrides of the general formula XH_2, i.e., OH_2, SH_2, SeH_2, TeH_2 and also PoH_2. But the heats of formation of H_2O (59 Kcal/mole) is much higher than any of the compounds H_2S, H_2Se, H_2Te. Water is a highly stable associated and neutral liquid. H_2S, H_2Se and H_2Te are gases having acidic properties and unpleasant odour and these are easily decomposed because of their reducing properties. The strength of acid behaviour and reducing power increases in the order :

$$H_2O < H_2S < H_2Se < H_2Te < H_2Po$$

But the thermal stability decreases from H_2O to H_2Po in the hydracid series. All these have similar structure of their molecules but due to the difference in the electronegativities of O,S, Se, Te, Po with that of H, and the increase in their ionic radii, the bond lengths and bond angles are not the same. H_2O shows hydrogen bonding due to much greater difference in the electronegativity values of O and H as compared to those between S and H and others. H_2S and H_2Te do not have the property of hydrogen bonding.



These factors give rise to difference in the properties of these compounds as given in Table 21.3.

Table 21.3. Properties of H_2O, H_2S H_2Se and H_2Te.

Hydride	*Melting point (°C)*	*Boiling point (°C)*	*Heat of formation Kcal/mole*	*Acid strength K_a*	*Remark*
H_2O	0	100	68	10^{-14}	Associated liquid (neutral)
H_2S	−86	−61	5	3×10^{-7}	weakly acidic
H_2Se	−60	−41	−19	2×10^{-4}	acidic
H_2Te	−51	−2	−34	10^{-2}	strongly acidic

(7) The double bond in O_2 is stronger than S—S or Te—Te bond. Hence oxygen can exist as separate molecular species as O_2. This is not the case with S, Se and Te although these may occur in nature in the free state but in the form of atomic aggregates and as the atomic number increases, these assume more pronounced metallic character with much higher melting and boiling points. Oxygen forms two double bonds whereas, S, Se and Te usually form two single bonds. Thus S forms S_8 ring in which each S has two single bonds. The three atoms of oxygen in O_3 is highly unstable.

(8) O_2 molecule has been found to have magnetic properties, which in the case of other members is not so pronounced.

(9) A marked characteristic of this group is the existence of a number of allotropic forms. In this property oxygen also shows likeness to other elements of this group.

(10) Photoelectric behaviour of Se is much more pronounced than Te and for this reason Se is on great demand for photo-electric tubes. Other elements of this group do not show this property.

Thus it can be inferred that oxygen as a member of the group VIA elements differs markedly in physical and chemical behaviours from S, Se and Te. The latter three elements have similar chemical properties with the usual gradations that is expected on account of the electronic configuration.

OXYGEN

Sources of oxygen : Oxygen is the most plentiful element in the earth's atmosphere, sea-water and the earth's crust. It is an essential element for all forms of life. Without oxygen no life can exist since it is required to convert the food materials to CO_2 and H_2O.

Preparation of oxygen :

1. By heating an unstable oxide :

$$2\,HgO \xrightarrow{heat} 2Hg + O_2$$

2. From peroxide : In metal peroxides and H_2O_2 oxygen has the unusual oxidation number of -1 and hence these are unstable compounds and decompose to evolve oxygen in zero oxidation state and also in -2 oxidation state. Thus :

$$2\,H_2O_2 \xrightarrow{heated} 2\,H_2O + O_2$$

$$(BaO + O_2 \xrightarrow[500°C]{heated} BaO_2)$$

$$BaO_2 \xrightarrow[700°C]{heated} BaO + O_2 \text{ (Brin's Process)}$$

Some reactions undergo swift decomposition when heated or in presence of other substances, e.g.,

$$2Na_2O_2 + 2H_2O \xrightarrow{heat} 4NaOH + O_2$$

3. From oxygen-rich compounds :

$$2KMnO_4 \xrightarrow{heat} K_2MnO_4 + MnO_2 + O_2$$

$$KClO_3 \xrightarrow[(MnO_2\ catalyst)]{heat} 2\,KCl + 3O_2$$

4. Electrolytic method : Water, containing a little acid or alkali when subject to electrolysis, evolves O_2 and H_2 at the anode and cathode respectively due to the following reactions :—

$$2H_2O + 2e \rightarrow 2H_2 + O_2$$

$$4(OH)^- \rightarrow 2H_2O + O_2 + 4e$$

5. From liquid air : Large quantities of oxygen are produced by the fractional evaporation of liquid air. Since the boiling point of liquid nitrogen is −196°C compared to −183°C for oxygen, nitrogen is volatilized away first by distillation of the liquid air leaving the residue of almost pure liquid oxygen (Claude's Process).

Properties of oxygen : The physical properties of oxygen have been shown in Table 21.2 and a list of chemical properties which are common is given below .

(1) Oxygen is an active element and combines with all the other elements either directly or by some other methods (exception—inert gases). The process of combination of oxygen with an element or compound is called oxidation because oxygen normally changes from zero valent state to O^{-2} state by accepting electrons. Some typical examples are given by the following equations :—

(a) With metals :

$$2Na + O_2 = Na_2O_2 \text{ (ordinary condition)}$$

$$2Mg + O_2 = 2MgO \text{ (heat)}$$

$$3Fe + 2O_2 = Fe_3O_4 \text{ (heat)}$$

(b) With non-metals :

$$2H_2 + O_2 = 2H_2O \text{ (burning)}$$

$$C + O_2 = CO_2 \text{ (burning)}$$

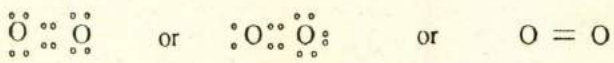
$$S + O_2 = SO_2 \text{ (burning)}$$

(c) With compounds :

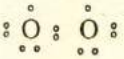
$$2H_2S + 3O_2 = 2H_2O + 2SO_2 \text{ (burning)}$$
$$CS_2 + 3O_2 = CO_2 + 2SO_2 \text{ (burning)}$$
$$2ZnS + 3O_2 = 2ZnO + 2SO_2 \text{ (burning)}$$
$$2CO + O_2 = 2CO_2 \text{ (burning)}$$
$$P_4O_6 + 2O_2 = P_4O_{10}$$

The Structure of Oxygen Molecule

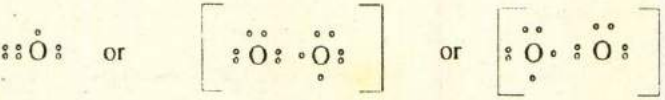
The structure of O_2 molecule has been represented as formed by sharing two pairs of electrons between the two O atoms in which all the electrons are paired :



But O_2 molecule has magnetic properties. It is attracted by a magnetic filed and calculations show that O_2 molecule has two single (unpaired) electrons. Therefore, the modified Lewis structure of O_2 molecule may be written as,



with one electron on each atom of oxygen. Pauling considered that O_2 is an odd molecule with three electron bonds as,



Each Lewis structure contain 12 electrons between the two oxygen atoms in O_2 molecule.

But from the point of view of molecular orbital method the O_2 molecule is formed by the overlap of two atomic oxygen orbitals having electronic configurations :

$$1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$$

Neglecting the non-bonding electrons of $1s^2$ and $2s^2$ and considering the overlap of **p** orbitals of one oxygen atom with **p** orbitals of another oxygen atom, we

find that there are 6 molecular orbitals by the LCAO of 2 oxygen atoms, each having 3 atomic 2p orbitals. Out of six molecular orbitals three will be bonding orbitals and three anti-bonding orbitals. When we distribute the 8 electrons of p orbitals from each O atom i.e. $(2p^4 + 2p^4)$ each of the molecular orbitals accommodate 2 electrons. Therefore, 6 electrons can be placed in the 3 bonding molecular orbitals leaving a balance of 2 electrons. Since the energy of the two anti-bonding orbitals are the same, the remaining two electrons are accommodated singly (unaired) in each of the two anti-bonding orbitals with parallel spins to have the maximum stability. Thus, these two unpaired electrons in the two anti-bonding molecular orbitals confer the magnetic properties to the O_2 molecule. This feature is diagrammatically shown in Fig. 21—1 showing the combination of three p orbitals of each oxygen atom.

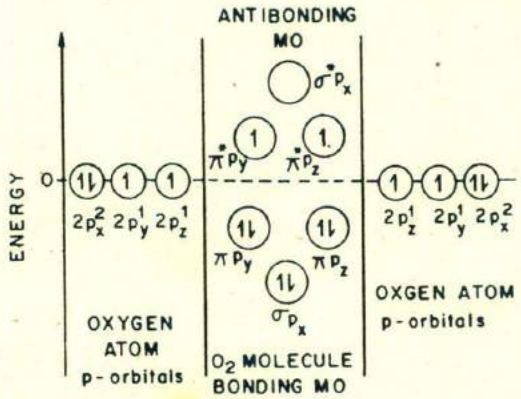


Fig. 21—1. Unpaired electrons in oxygen molecule in π^*p_y and π^*p_z orbitals.

Atomic Oxygen

At the ordinary conditions O_2 is slow to react possibly because the breaking of the O—O bond is rather difficult. In order to separate O_2 molecule into O atoms, 118 Kcal/mole of energy is required :

$$O_2 + 118 \text{ Kcal} = O + O$$

Hence O—O bond is rather strong. But at the elevated temperature O_2 is very reactive. At the ordinary temperature O_2 reacts with some substances

without bond breaking. Thus, Na_2O_2 and BaO_2 are formed in which O—O bonds remain unbroken.

The oxygen molecule can be broken up into atoms by ultraviolet radiation or by electron discharge. The atomic oxygen so produced is very reactive and releases more energy when reacting. The reactivity of atomic oxygen is indicated in its oxidation potential O/O^{-2}. This is greater than that of ozone or oxygen fluoride, OF_2, and is about the same as that of F_2 (–2.85V).

Uses of oxygen : (1) Metabolic process of respiration. (2) O_2-enriched air to patients with serious ailment. (3) In combination of fuels. (4) Metallurgical operations. (5) Cutting and welding metals with oxyhydrogen or oxyacetylene flames. (6) Oxygen masks for high altitudes. (7) Heavier isotopes of oxygen O^{18} are particularly used in tracer experiments for determining the structures of compounds.

OZONE

Ozone (O_3) is an allotropic form of O_2. Higher regions of atomosphere contain molecules of O_3. Generally referred to as the ozone layer.

Preparation : Ozone can be prepared in a number of ways. The main principle of the formation of ozone is to subject O_2 to an electric discharge. It is probable that atomic oxygen first formed combines with O_2 to give O_3.

There are various forms of apparatus used for the preparation and industrial production of ozone. These are known as *Ozonizers* which consist mainly of two electrically charged plates between which dry oxygen is passed. The gaseous products formed decrease in volume and possesses a pungent odour with a pale blue colour.

The formation of ozone from oxygen is an endothermic reaction and energy may be provided by means of electronic discharge. But other forms of energy may produce slight amount of ozone. Thus heat, ultraviolet light, slow oxidation of phosphorus, a jet of burning hydrogen during thunderstorm also form little ozone. Also, when F_2 reacts with water at low temperature, O_3 is formed :

$$3H_2O + 3F_2 = 6HF + O_3$$

Properties of Ozone

Physical properties : It is a pale blue gas with a pungent odour. The gas itself is colourless but it absorbs light strongly in the ultraviolet region and for this reason upper atmosphere appears to be blue. O_3 thus acts as a shield by absorbing the deadly ultraviolet light for the earth's living beings. It is an allotropic form of oxygen. Due to high concentrations of industrial gases there is nowadays depletion of ozone layer of the atmosphere. This has been a case of great concern world-wide.

Chemical properties : O_3 is an unstable molecule because it is formed by endothermic reaction and hence it tends to lose energy by decomposition :

$$2O_3 = 3O_2 + 69 \text{ Kcal}$$

Ozone is, therefore, one of the most powerful oxidizing agents known. Only F_2, F_2O and atomic O stand above O_3 in oxidizing power.

The following oxidation reactions may be cited as examples of oxidizing nature of O_3 :

$$2KI + H_2O + O_3 = 2KOH + I_2 + O_2$$

$$2HCl + O_3 = H_2O + Cl_2 + O_2$$

$$PbS + 4O_3 = PbSO_4 + 4O_2$$

$$N_2O_4 + O_3 = N_2O_5 + O_2$$

$$3SO_2 + O_3 = 3SO_3$$

$$3SnCl_2 + O_3 + 6HCl = 3SnCl_4 + 3H_2O$$

$$H_2O_2 + O_3 = H_2O + 2O_2$$

$$Ag + O_3 = AgO + O_2$$

$$Hg + O_3 = HgO + O_2$$

$$I_2 + 5O_3 + H_2O = 2HIO_3 + 5O_2$$

Unsaturated organic molecules form explosive compounds called ozonides, O_3 combines at the double bond. C_2H_4 gives ethylene ozonide :

$$H_2C{=}CH_2 + O_3 \quad = \quad \begin{array}{c} CH_2{-}O \\ O \\ CH_2{-}O \end{array}$$

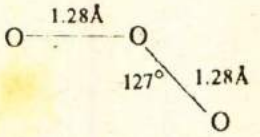
ethylene ozonide

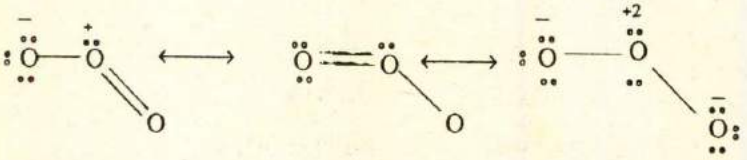
Recently ozonates, KO_3, CsO_3, have also been prepared. Distinctions between O_3, O_2 and H_2O_2 are given below :—

Reagent	O_2	O_3	H_2O_2
Hg	No reaction	HgO	×
$KMnO_4$ soln.	×	×	Mn^{+2} formed
H_2CrO_4	×	×	Cr^{+3} formed
Rubber	×	Brittle	No immediate action

Structure of O_3 : Previously O_3 was considered to be formed by the combination of three oxygen atoms so that each oxygen atom shared a pair of electrons with two others giving a triangular structure. But ozone is paramagnetic and the angle between three oxygen has been fond to be 127°. Therefore, the true structure must have two unpaired electrons in O_3 as in O_2 :







But the microwave technique has proved that the angle is only about 127° and each O—O distance is about 1.28Å.

SULPHUR

Sources of Sulphur

(1) Sulphur has been known from ancient time since it occurs free in nature in the solid state, particularly in volcanic regions of the earth. Volcanic gases also contain H_2S. and SO_2 which come in contact on the surface leading to their interaction and sulphur is precipitated which melts but solidifies when the volcanoes become extinct.

(2) Free sulphur also occurs in mines in the U.S.A and Mexico under the earth's surface about 700—900 feet below.

(3) In combined state sulphur is widely distributed in various compounds. The important ores of sulphur are :—

Iron pyrites	—	FeS_2
Copper pyrites	—	Cu_2S, FeS_2
Galena	—	PbS
Orpiment	—	As_2S_3
Cinnabar	—	HgS
Gypsum	—	$CaSO_4.2H_2O$

It may be noted here that the sulphide ores, such as PbS, HgS, Cu_2S, FeS_2 etc., contain small quantities of selenium and tellurium in the form of PbSe, HgSe and also in the free state in sulphur. Tellurium also occurs free along with Cu, Ag, Au and also as silver and gold tellurides (sylvanite,Ag_2Te, Au_3Te_3).

Extraction of Sulphur

Depending upon the source, various methods are being used for the extraction of elementary sulphur.

1. Frasch Process: This process is employed for underground sulphur in Lousiana, U. S. A. A drill-hole is made through which four concentric pipes are passed upto the sulphur-bearing bed. Superheated steam under pressure is forced down the next to the outermost of the four pipes. The hot steam melts the

sulphur. The compressed air is forced through the innermost pipe. The molten sulphur mixed with steam and air forms light emulsion which readily flows up through the third pipe. The outermost pipe serves as an outlet for superheated steam. The emulsified sulphur is conveyed to large settling tanks where it solidifies upon cooling. Frasch method gives very pure sulphur, almost 99.9% pure, and no further purification is required.

2. The Sicilian Method : In Sicily sulphur is found mixed with quartz and gypsum. The method of extraction of crude sulphur from this source consists in heating the lumps of the ore in a heap in closed chambers. Sulphur melts and runs off at the base.

Refining of sulphur is done by boiling sulphur in closed iron retorts and sulpur vapour is condensed in a large chamber in the form of fine particles known as *flowers of sulphur*. This melts at higher temperature and the molten sulphur is rolled into mould to give *roll sulphur* or *brimstone*.

3. From coal gas : Coal gas contains H_2S which is removed by passing the gas over heated Fe_2O_3 when FeS and Fe_2S_3 are formed. The mixture of FeS and Fe_2S_3 is known as *spent oxide*. When the spent oxide is exposed to the weathering conditions of air and water vapour, elementary sulphur is deposited :

$$Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O$$

$$2Fe_2S_3 + 3O_2 + 2H_2O = 2F_2O_3 + 6S$$

4. From CaS : Sulphur is also recovered from CaS which is formed during the manufacture of Na_2CO_3 by Le Blanc Process. This is done by liberating H_2S from CaS in water suspension by means of CO_2. H_2S mixed with air passed over heated Fe_2O_3 gives elementary sulphur :

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S$$

$$2H_2S + O_2 = 2S + 2H_2O$$

5. By bacterial action : Certain bacteria have the remarkable property of converting sulphates to elementary sulphur. Calcium sulphates have been converted to free sulphur by the artificially prepared strains of bacteria.

.6. ***From roasting of sulphides*** : It is to be noted that the sulphide ores are not used for extraction of sulphur. These are roasted for the extraction of metals and SO_2 formed is mainly used for the manufacture of H_2SO_4. But sometimes it becomes necessary to reduce SO_2 to S by passing the gases through coke heated at 1100°C when the reaction $SO_2 + C = CO_2 + S$ produces S. Also on roasting the sulphide ores contaminated with selenium, both SO_2 and SeO_2 are formed. But SeO_2 is reduced by SO_2 giving fine powder of free selenium in the flue gas from which it is precipitated by electrical cottrell precipitator :

$$SeO_2 + 2SO_2 = 2SO_3 + Se$$

Selenium is also recovered from the metal oxide formed, and from the anode mud obtained during the electrolytic refining of copper.

Properties of Sulphur

Physical properties : The electronic configurations and other physical constants have been listed in Table 21.2. An interesting feature is the well-marked property of sulphur in having several allotropic forms as is the case with O, Se and also to some extent in Te.

Allotropic forms of sulphur : Sulphur exists in a variety of forms—in the solid, liquid and gaseous states.

Solid sulphur : Several crystalline forms of sulphur are known. At room temperature the solid sulphur has rhombic form and is the stablest form of sulphur composed of S_8 molecules. This is also known as octahedral or *α-sulphur*. Each S atom in S_8 molecule has two single bonds and thus forms an eight-membered ring. The molecule is puckered, i.e., four S atoms lie in one plane and the four S atoms lie in another plane. The structure of S_8 molecule is shown in Fig. 21—2.

On heating rhombic sulphur below 100°C, it is changed to monoclinic form. This also consists of S_8 molecules which are arranged in a different geometric form. This is also known are as *prismatic* or *β-sulphur*. The transition temperature from rhombic to monoclinic form contains more energy and at lower temperature or room temperature it tends to convert itself to the rhombic form.

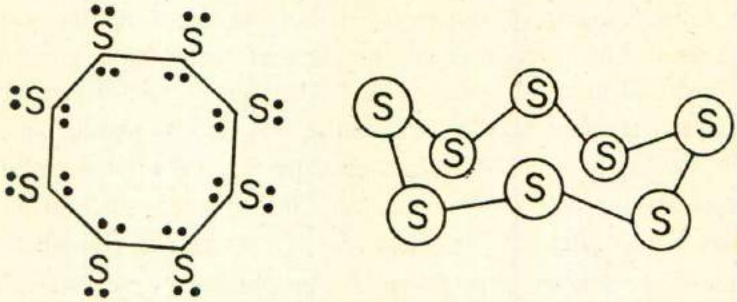
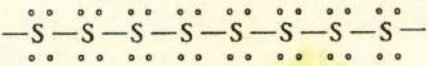


Fig. 21—2. Structure of S_8 molecule in sulphur, (a) Electron arrangement in S_8 molecule ; (b) "Puckered" arrangement of 8 S atoms.

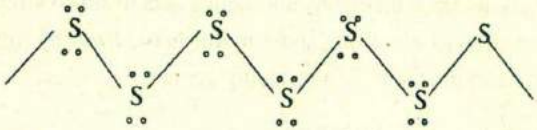
Both rhombic and monoclinic sulphurs are insoluble in water but soluble in CS_2, S_2Cl_2 etc. But the monoclinic form has greater solubility than the rhombic form. Their molecular weights have been determined both in the vapour state and in solutions.

Liquid sulphur : On heating solid sulphur to just above the melting point (119°C), a clear straw-coloured mobile liquid is formed. This also contains S_8 molecules. As the temperature is raised, the S_8 ring of the yellow mobile sulphur is present as long open chains of S atoms known as *λ-sulphur* :



On further heating the liquid gradually darkness and becomes very viscous at above 200°C when it gives a thick gum-like mass with darkend colour. The long chains of S atoms become entangled with each other as the temperature is raised above 200°C indicated by the increased viscosity. This darkend form of liquid sulphur is known as *μ-sulphur*.

When the yellow mobile liquid, *λ-sulphur*, is suddenly cooled to room temperature by pouring it into water, a rubber-like material is formed which is known as *plastic sulphur*. The long chains of S atoms become oriented in a zig-zag manner of indefinite lengths which imparts the elastic rubber-like property. The plastic sulphur is insoluble in CS_2. Upon standing, plastic sulphur, like all other forms of sulphur, changes to the rhombic sulphur :



Sulphur vapour : Sulphur boils at 444.6°C and molecular breakdown occurs in the vapour state consisting of S_8, S_6, S_2 molecules both in the cyclic ring form and open chain form. At the boiling point (in equilibrium with the liquid sulphur) the sulphur vapour is red due to the lone electrons on each sulphur atom. At above 1000°C, the rings and chains of sulphur atoms break down and the vapour consists of S_2 molecules and is of yellow colour. At about 2000°C, S_2 dissociates to give atomic S to some extent.

Some other forms of sulphur : When elementary S is precipitated out from Ca-Thiosulphate or polysulphide by means of HCl, a white amorphous product is obtained which is known as *milk of sulphur* soluble in CS_2 :

$$CaS_5 + 2HCl = CaCl_2 + H_2S + 4S$$

Colloidal sulphur is formed when H_2S ans SO_2 react together in aqueous solution or when sodium thiosulphate is decomposed by a solution of H_2SO_4. Sulphur remains in a clear yellow solution and can be coagulated by adding electrolytes, such as alum solution.

It may be noted that several allotropic forms of selenium contains zig-zag chains of selenium atoms in the solid state. Red and black forms of selenium are also known. Tellurium is a brittle silvery white metal and an amorphous form of tellurium also exists.

Chemical properties : Although the elements O, S, Se, Te and Po form one group, the chemistry of O and Po are so different that these are considered separately. But the sulphur family having S, Se and Te have the general gradation of group characteristics and have almost similar chemistry.

Elementary sulphur, although a non-metallic stable solid, is quite reactive. Many metals react with S at ordinary temperature, e.g., Hg on rubbing with sulphur powder forms HgS. Elementary S is both an oxidizing and a reducing agent. S containing s^2p^4 electrons has a tendency to form the stable s^2p^6

arrangement by taking up 2 electrons and hence acts as an oxidizing agent. The oxidation involves loss of electrons and sulphur is oxidized by most non-metals to + 4 or + 6 state and thus acts as a reducing agent.

Oxidizing Properties of Sulphur

(a) Reaction with H_2 : Sulphur reacts directly with H_2 forming H_2S :

$$H_2 + S \rightleftharpoons H_2S$$

The proportions of H_2S formed increase with the increase of temperature.

(b) Reaction with non-metals : C at elevated temperature forms CS_2:

$$C + 2S \rightleftharpoons CS_2$$

(c) Reactions with metals : Metals, such as Zn, Al, Fe, on gently heating with S, form metal sulphides :

$$Zn + S = ZnS$$

$$Fe + S = FeS$$

It may be noted that properties of sulphides containing S^{-2} ion are quite different form the corresponding oxides containing O^{-2} ions.

Reducing Properties of Sulphur

When sulphur reacts with non-metals which are more electronegative than sulphur, it assumes the oxidation state of + 4 or + 6.

(a) Reaction with O_2 : Sulphur burns in air (O_2) with a blue flame forming SO_2 and traces of SO_3 (about 3—4%) :

$$S + O_2 = SO_2$$

$$2SO_2 + O_2 = 2SO_3$$

These are very important reactions industrially and will be described in connection with H_2SO_4.

It has been noticed that S, when exposed to moist air, is slowly oxidized to give H_2SO_4 :

$$2S + 2H_2O + 3O_2 = 2H_2SO_4$$

(b) Reaction with halogens : Sulphur forms a large number of halides by direct union with halogens except iodine:

$S + F_2 \rightarrow S_2F_2$, SF_4, SF_6, S_2F_{10} $\quad S + Cl_2 \rightarrow S_2Cl_2$, SCl_2, SCl_4 $\quad S + Br_2 \rightarrow S_2Br_2$

(c) Reaction with HNO_3 and H_2SO_4 (Concentrated and hot condition):

$$S + 6HNO_3 = H_2SO_4 + 2H_2O + 6NO_2$$

$$S + 2H_2SO_4 = 2H_2O + 3SO_2$$

(d) Reaction with alkali : Both S^{-2} and thiosulphates are formed when S is boiled with alkalies :

$$4S + 6NaOH = Na_2S_2O_3 + 2Na_2S + 3H_2O$$

N.B. Selenium more or less has similar reactions but is a weaker oxidizing and weaker reducing agent than sulphur.

Uses of S, Se and Te

Sulphur : (1) Production of sulphuric acid, one of the basic materials for many industries.

(2) SO_2 from S is used for industrial bleaching purpose.

(3) Production of CS_2, an industrial solvent.

(4) S in vulcanization of rubber.

(5) Gunpowder, explosive and a host of other compounds of sulphur.

Selenium and its compounds are used in :

(1) Electronic industries as an efficient rectifier.

(2) Producing colourless glass which is generally coloured green due to iron silicate.

Some Important Compounds of Sulphur

Hydrogen sulphide, H_2S : It is a quite familiar gas. It is much used in the laboratory for qualitative analysis.

(1) It is generally prepared in Kipps' apparatus by the reaction of FeS with dilute H_2SO_4 or HCl :

$$FeS + H_2SO_4 = FeSO_4 + H_2S$$

H_2S prepared by the above method is impure.

(2) Pure H_2S may be obtained by the hydrolysis of sulphides of more electropositive metals, such as Al_2S_3, or by the action of dilute HCl on NaHS :

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S$$

$$NaHS + HCl = H_2S + NaCl$$

(3) Recently a convenient and less obnoxious source of H_2S has been found in some sulphur-containing organic compounds, such as methyl thioacetamide (Methyl thiorurea), CH_3CSNH_2. Whenever H_2S is required, a pinch of this substance in water gives H_2S and ammonium acetate by hydrolysis :

$$CH_3CSNH_2 + 2H_2O = CH_3COONH_4 + H_2S$$

The hydrolysis is very rapid in hot solutions.

Properties of H_2S : (1) It is a colourless gas having the smell of rotten eggs. (2) It is highly poisonous. (3) It can be condensed to a colourless liquid at –60°C (and solidifies at –86°C).

Aqueous solution of H_2S : H_2S is moderately soluble in water and the aqueous solution is freely acidic. It ionizes as :

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^- \qquad Ka_1 = 3 \times 10^{-7} \text{ at } 20°C$$

$$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{-2} \qquad Ka_2 = 2 \times 10^{-16} \text{ at } 20°C$$

When the aqueous solution is exposed for a long time to the action of air, sulphur is precipitated out due to aerial oxidation of H_2S :

Reducing properties of H_2S : The sulphur in H_2S readily gives up the electrons and becomes oxidized to S, S^{-4} S^{+6} depending upon the conditions and the nature of the other substances which react with it. H_2S burns in air to form SO_2 and when the air is insufficient, only S is formed. In presence of strong oxidizing agents in excess, H_2S may be oxidized to H_2SO_4 :

$$2H_2S + 3O_2 = 2H_2O + 2SO_2$$

$$2H_2S + O_2 = 2H_2O + 2S$$

$$H_2S + 4Br_2 + 4H_2O = H_2SO_4 + 8HBr$$

In aqueous acid solutions H_2S reduces Fe^{+3} to Fe^{+2}, I_2 to I^-, MnO_4^- to Mn^{+2}, $Cr_2O_7^{-2}$ to Cr^{+3}, HNO_3 to NO. In all these reactions, H_2S is oxidized to free sulphur in aqueous solutions :

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$$

$$5H_2S + 2KMnO_4 + 3H_2SO_4 = 5S + 2MnSO_4 + 8H_2O + K_2SO_4$$

Precipitating action of H_2S : The importance of H_2S in analytical chemistry lies in the fact that it precipitates metal sulphides from acidic, neutral and alkaline solutions. These metal sulphides show a wide variation in solubility and thus can be divided into several analytical groups. For instance, CuS, PbS and CdS are insoluble in dilute HCl. Others, such as ZnS, are soluble in dilute HCl but insoluble in NH_4OH solution.

The most important factor which enables the use of H_2S in qualitative analysis is the control of S^{-2} ion concentration in the solution. In an aqueous solution containing a number of metal ions M^{+2} and sulphide ions S^{-2}, a metal sulphide MS will be precipitated only if the product of the concentrations of the S^{-2} ion and M^{+2} ion (raised to their appropriate powers) exceeds the solubility product constant, K*sp* of the metal sulphides. Thus :

If $[M^{+2}] \times [S^{-2}] > K_{sp}$—metal sulphide is precipitated.

$[M^{+2}] \times [S^{-2}] < K_{sp}$—metal sulphide is not precipitated.

The S^{-2} ion concentration can be easily controlled to achieve the above condition. The reactions are based on the equilibrium dissociation of H_2S as :

$$H_2S \rightleftharpoons HS^- + H^+$$

$$HS^- \rightleftharpoons H^+ + S^{-2}$$

and the solubility of metal sulphide as represented by the equilibrium equation :

$$MS\ (\text{solid}) + 2H^+ \rightleftharpoons M^{+2} + H_2S\ (\text{gas})$$

The solubility of a metal sulphide according to the equilibrium equation depends upon the following factors :—

1. *The solubility of the solid in water* : The greater the solubility, the greater the equilibrium displaced towards the right of the equilibrium equation. This also gives greater solubility in acid. CoS ($K_{sp} = 1\times10^{-21}$) is more soluble in water than CuS ($K_{sp} = 1\times10^{-25}$). K_{sp} of CuS > K_{sp} of CoS. This is also true for acid solution. In 2N HCl, it is only CuS which is precipitated out but CoS remains in solution.

2. *The concentration of acid* : H^+ occurs in the left of the equation. It is natural that increased concentration of H^+ lead to greater solubility of MS. Decreasing the concentration therefore, precipitate out the more soluble metal sulphide. It is for this reason that CoS and ZnS are precipitated out by H_2S in alkaline solution (decreasing the H^+ ions by adding OH^- ion in the form of NH_4OH).

3. *The strength of the weak acid formed* : The weaker the acid formed the more soluble the salt is in the strong acid. For instance, most heavy metal carbonates are easily soluble in dilute mineral acid because of the formation of H_2CO_3 a weak acid, during the reaction. The reason that some heavy metal sulphides are not soluble in mineral acids is due to the crystal structure.

Thus we can see that by adding H^+ from outside (HCl as usual) the concentration of S^{-2} ion is reduced and under this condition only sulphides of analytical Group II metals, such as CuS, PbS, CdS, Bi_2S_3 etc. precipitated because their K_{sp} values are very small. ZnS, MnS, NiS etc. are not precipitated under this condition because their K_{sp} values are very high, These can be precipitated if S^{-2} ion concentration is increased by decreasing H^+ ions (usually by adding NH_4OH or OH^- ions) as in the case of Zn, Mn, Co, Ni etc. metal ions of the analytical group.

Test for H_2S or Sulphides : A paper moistened with lead acetate solution turns black on exposure to H_2S due to the formation of black PbS. In solution S^{-2} ion is detected by sodium nitroprusside which gives violet colour in presence of S^{-2} ion :

$$2Na_2[Fe(CN)_5\,NO] + H_2S \rightarrow Na_4\,[Fe\,(CN)_5NOS]_2 + H_2O$$

Uses of H_2S : (1) It is a versatile analytical reagent and is used for classification of metals into different groups in analytical chemistry identification tests and separation procedures. (2) In synthetic work for the preparation of sulphur containing compounds.

Sulphides : Normally the diprotic H_2S forms two series of sulphides (so also H_2Se and H_2Te). Normal sulphides and hydro-sulphides of metals are well-known and have been dealt in appropriate chapters. These sulphides are formed from H_2S in solution or by direct reactions of metal and sulphur.

It has been found that only very slightly soluble sulphides can exist in the presence of water. This is because of the strong tendency of the S^{-2} and HS^- ions to act as proton acceptors. The soluble ionic sulphides BaS, Na_2S, K_2S etc. are readily hydrolysed into HS^- and OH^- and in some cases to H_2S (as in the case of Al_2S_3, Cr_2S_3 etc.

$$S^{-2} + H_2O \rightleftharpoons HS^- + OH^-$$

$$HS^- + H_2O \rightleftharpoons H_2S + OH^-$$

Aqueous solutions of such sulphides are alkaline. As_4S_6 is not hydrolysed because it is insoluble. Sulphides of Al, Cr, Fe cannot be prepared in aqueous media because of hydrolysis.

Some of the coloured sulphides, such as FeS_2, PbS etc., prepared under controlled condition resemble alloys in their properties. They exhibit metallic lustre and conduct electricity in the solid state. This is due to delocalization of some of the electrons in the structure of metal sulphides as is the case in metals and also in graphite. The selenides have similar structures.

Polysulphides :When sulphur is boiled with an alkali solution or a soluble sulphide, polysulphide ions are obtained. The resulting solution is yellow or orange-red in colour. Acidification of the polysulphides gives a mixture of hydrogen polysulphides, H_2Sx, where X = 1, 2, 3, 4, 5, 6. The combination of S with S^{-2} ions may be represented as,

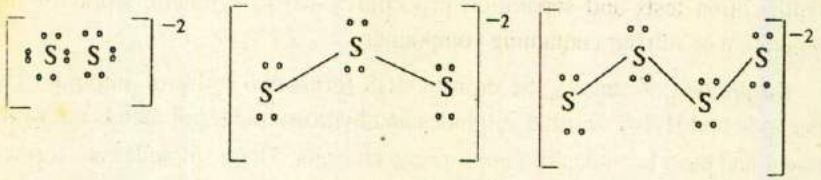
$$S + S^{-2} \rightleftharpoons S_2^{-2}$$

$$2S + S^{-2} \rightleftharpoons S_3^{-2}$$

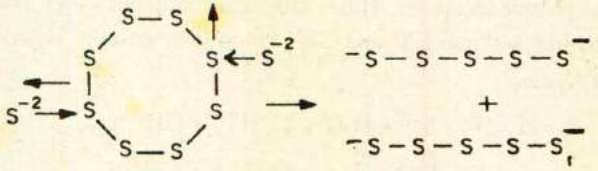
$$3S + S^{-2} \rightleftharpoons S_4^{-2}$$

$$4S + S^{-2} \rightleftharpoons S_5^{-2}$$

H_2S_2 is called hydrogen persulphide as an analogue of H_2O_2.



A mechanism suggesting the breaking open of the S_8 ring in sulphur by S^{-2} ion has been put forward as :



The polysulphide ions, like the peroxide ion, are oxidizing agents. Most of the metal sulphides are oxidized to the thiocomplexes :

$$As_2S_3 + 5S^{-2} \rightleftharpoons 2AsS_4^{-3}$$

$$Sb_2S_3 + 5S^{-2} \rightleftharpoons 2SbS_4^{-3}$$

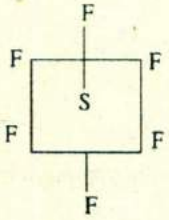
$$SnS_2 + S^{-2} \rightleftharpoons SnS_3^{-2}$$

In alkaline solutions in the absence of excess polysulphide ion the polysulphide chain is unstable and breaks down to give elementary S and simple sulphides :

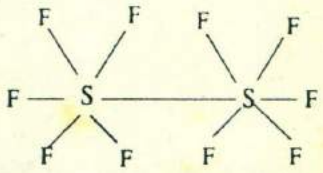
$$2AsS_4^{-3} \rightarrow 5S + As_2S_3$$

Sulphur hexafluoride, SF_6 : This is most remarkable sulphur halide. It is formed when S burn in F_2. Along with SF_6 some lower fluorides of S are also formed. These may be removed by liquefaction and fractional distillation. SF_6 is an inert gaseous substance and is not affected by any reagent, acid, alkali metals etc. It is the most inert sulphur compound known. The larger S atom (as compared to oxygen) has **d** orbitals available which can be used in covalent

bond formation. SF_6 is an octahedral molecule with S atom at the centre of the octahedron and the 6F atoms situated at the 6 corners of the octahedron. The inertness is possibly due to *steric hinderance* by which S atom in SF_6 is protected. An stable S_2F_{10} formed in small amount along with SF_6 has been separated from the liquid by fractionation. S_2F_{10} is less inert than SF_6 possibly due to S—S bond.



SF_6



S_2F_{10}

SF_6 finds application as electrical insulator at very high temperature.

ScF_6 and TeF_6 are more reactive than SF_6 and are prepared from the elements.

Sulphur monochloride, S_2Cl_2 : This is the most important halide of sulphur and finds application in rubber industry for vulcanization. This is obtained by several processes :—

(a) Chlorination of S in limited amount of Cl_2 :

$$2S + Cl_2 = S_2Cl_2$$

(b) When thionyl chloride, $SOCl_2$, or sulphuryl chloride, SO_2Cl_2, are heated with sulphur :

$$2SOCl_2 + 3S = 2S_2Cl_2 + SO_2$$

$$SO_2Cl_2 + 2S = S_2Cl_2 + SO_2$$

(c) It is obtained as a by-product when CCl_4 is manufactured from CS_2 and Cl_2 :

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2$$

S_2Cl_2 is an orange-yellow oily liquid readily hydrolysed by water accompanied by self-oxidation forming elementary S and SO_2 :

$$2S_2Cl_2 + 2H_2O = SO_2 + 2HCl + 2S$$

S_2Cl_2 has the same structure as H_2O_2 :



S_2Cl_2 is a good solvent for S, I_2 and many organic compounds. It reacts with C_2H_4 to give mustard gas :

$$S_2Cl_2 + 2C_2H_4 \rightarrow Cl\text{–}CH_2\text{–}CH_2\text{–}S\text{–}CH_2\text{–}CH_2\text{–}Cl + S$$

Sulphur dichloride, SCl_2 : This is obtained by further chlorination of S_2Cl_2 in the form of a dark coloured liquide :

$$S_2Cl_2 + Cl_2 = 2SCl_2$$

Further chlorination also gives SCl_4.

Sulphur oxychlorides : SO_2Cl_2 and $SOCl_2$ are known as *sulphuryl chloride* and *thionyl chloride* respectively.

Thionyl chloride, $SOCl_2$, is a colourless liquid and prepared readily from PCl_5 and SO_2. It can also be prepared from $COCl_2$ and SO_2 :

$$SO_2 + PCl_5 = SOCl_2 + POCl_3$$

$$COCl_2 + SO_2 = SOCl_2 + CO_2$$

$SOCl_2$ is an important reagent in organic chemistry and is used to convert carboxylic acid to their acid chlorides and SO_2 gas is out :

$$SOCl_2 + R\text{—}COOH = R\text{—}COCl + SO_2 + HCl$$

The structure of $SOCl_2$ is related to H_2SO_3.

Sulphuryl chloride, SO_2Cl_2, is obtained as a liquid by direct combination of SO_2 with liquid Cl_2 in presence of a catalyst (camphor) :

$$SO_2 + Cl_2 = SO_2Cl_2$$

and also from H_2SO_4 and PCl_5 :

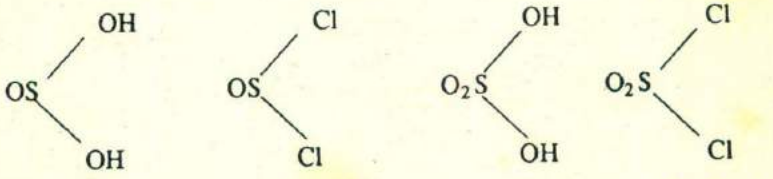
$$H_2SO_4 + 2PCl_5 = SO_2Cl_2 + 2POCl_3 + 2HCl$$

Both SO_2Cl_2 and $SOCl_2$ are hydrolysed in water forming H_2SO_4 and H_2SO_3 respectively :

$$SO_2Cl_2 + 2HOH \rightarrow SO_2(OH)_2 + 2HCl$$

$$SOCl_2 + 2HOH \rightarrow SO(OH)_2 + 2HCl$$

Hence, structurally these are related to H_2SO_4 and H_2SO_3 :



Sulphurous acid — Thionyl chloride — Sulphuric acid — Sulphuryl chloride

Oxides of sulphur : In the sulphur family, S forms more numerous oxides. These are :

SO	—	sulphur monoxide
S_2O_3	—	sulphur sesqioxide
SO_2	—	sulphur dioxide
SO_3	—	sulphur trioxide
S_2O_7	—	sulphur heptoxide
SO_4	—	sulphur tetroxide

Of the above six sulphur oxides, only SO_2 and SO_3 are important. Others are unstable and unimportant.

Sulphur Dioxide, SO_2

This is of considerable technological importance and is obtained by various methods :

(a) By burning sulphur (brimstone) in air :

$$S + O_2 = SO_2$$

(b) By roasting of pyrites and other metal sulphides :

$$4FeS_2 + 11\,O_2 = 2Fe_2O_3 + 8SO_2$$

$$2ZnS + 3\,O_2 = 2ZnO + 2SO_2$$

(c) By reducing H_2SO_4 with metals or non-metals :

$$2H_2SO_4 + Cu = CuSO_4 + SO_2 + 2H_2O$$

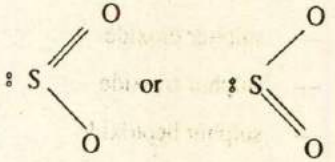
$$2H_2SO_4 + S = 3SO_2 + 2H_2O$$

(d) By the action of dilute acids on sulphits or bisulphites :

$$Na_2SO_3 + 2HCl = SO_2 + 2NaCl + H_2O$$

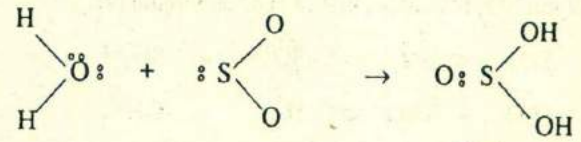
Properties : It is a colourless gas with choking smell. It readily condenses to liquid SO_2 at $-10°C$ and freezes at $-72.7°C$.

The properties of SO_2 is best understood from the structure of its molecule. SO_2 gas has a large value of dipole moment indicating O—S—O bond to be non-liner. The contributing structures may be written as,

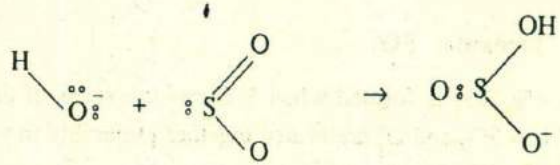


The structure confers on SO_2 four-fold properties : (1) Lewis acid, (2) Lewis base, (3) reducing agent, (4) oxidizing agent.

1) As Lewis acid :

(a) 

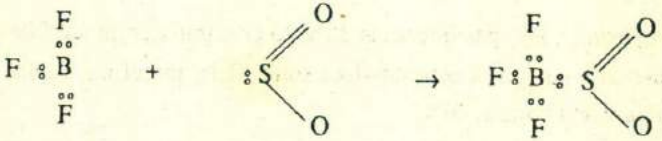
Sulphurous acid

(b) 

HSO_3^- ion

(c) $CaO + SO_2 \rightarrow CaSO_3$

(2) As Lewis base :



(3) Oxidizing agent :

$$2H_2S + SO_2 = 3S + 2H_2O$$

(4) Reducing agent : SO_2 is most important as a reducing agent in most chemical reactions. Its bleaching property is attributed due to the reducing action of SO_2 in presence of H_2O (i.e., of H_2SO_3) as compared to chlorine which bleaches by oxidation. As reducing agent SO_2 liberates I_2 from KIO_3, decolourises $KMnO_4$ and turns $K_2Cr_2O_7$, green.

Uses of SO_2 : (1) Bleaching of paper, silk, wool etc. (2) Preservative for dried fruits. (3) Largely used for the manufacture of H_2SO_4. (4) In petroleum industry for bleaching of kerosene. (5) Liquid SO_2 is used as a refrigerant. (6) Liquid SO_2 as a non-aqueous solvent.

Liquid SO_2 : It conducts electricity and is a good solvent for a number of ionic compounds and is used for carrying out chemical reactions. The auto-oxidation of liquid SO_2 resembles that of H_2O and liquid NH_3:

$$SO_2 + SO_2 \rightleftharpoons SO^{+2} + SO_3^{-2}$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

Sulphur Trioxide, SO_3

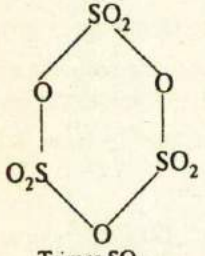
About 3—4% SO_3 is formed when S Burns in excess of air producing mainly SO_2. When SO_2 and O_2 are heated together preferably in presence of a catalyst, such as Pt or V_2O_5 giving SO_3 :

$$2\,SO_2 + O_2 \underset{V_2O_5}{\overset{Pt}{\rightleftharpoons}} 2SO_3 + 45\ Kcal$$

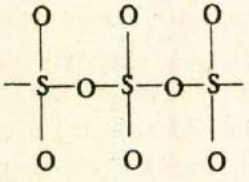
SO_3 is the dehydrated product of H_2SO_4 and can be obtained by gently distilling H_2SO_4 preferably with an excess of P_2O_5 :

Properties : SO_3 gas freezes at 15°C to give transparent ice-like crystals. On exposure to air it gives asbestos-like solid. It is, therefore, liquid at ordinary temperature and boils at 46°C.

The three solid forms of SO_3 consist of (1) trimer $(SO_3)_3$, ice-like, (2) long-chain, SO_3 groups, asbestos-like, (3) long-chain SO_3 groups joined in layers (unstable form) :



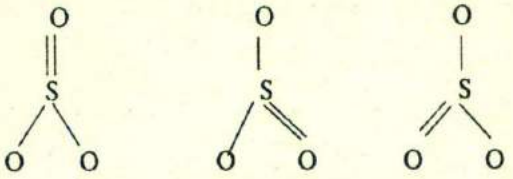
Trimer SO_3



Chain SO_3

Stabilized SO_3 are now being sold commercially under the trade name of *Sulphans*.

In the vapour state SO_3 is a monomer (consisting of only one molecule). In the solid state it has several structural modification as mentioned. Liquid SO_3 mainly consists of three molecules of SO_3 (trimer) joined together in 6-membered ring. In the single molecule the oxygen atoms occupy the three corners of an equilateral triangle with S atom at the centre :

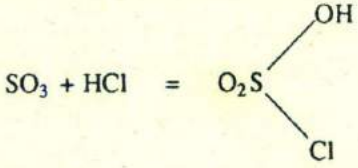


SO_3 is the strongest Lewis acid. It reacts almost vigorously with bases, such as H_2O, amines, ethers, oxides etc. :

$$SO_3 + H_2O = H_2SO_4 + 45\ Kcal$$

$$SO_3 + BaO = BaSO_4$$

It also reacts with non-basic substances, such as HCl, H_2SO_4 :



$SO_3 + HCl = O_2S(OH)Cl$ (Chlorosulphonic acid)

$$SO_3 + H_2SO_4 = H_2S_2O_7 \quad \text{(Pyrosulphuric acid)}$$

The pyrosulphuric acid (disulphuric acid) along with more polymerised forms, $H_2S_3O_{10}$ and $H_2S_4O_{13}$, gives rise to the familiar *fuming sulphuric acid* or *oleum*.

OXYACIDS OF SULPHUR

Oxyacids of sulphur contain S atom in the oxidation states from +2, +3, +4 and +6. A very large number of oxyacids of sulphur is known. On the basis of their nomenclature, some of these may be classified into the following groups:—

(I) Normal oxyacids : These are well-known acids :

H_2SO_3 H_2SO_4

(II) Pyroacids : These are formed from H_2SO_3 or H_2SO_4 generally by condensation reaction :

$$H_2S_2O_5 \qquad H_2S_2O_7$$

(III) Thioacids : These again consist of—

(a) Thionic acids : $H_2S_xO_6$ where x = 2 to 6

(b) Thionous or hyposulphurous : $H_2S_2O_4$

(c) Thiosulphuric acid : $H_2S_2O_3$

(IV) Peroxyacids : These contain—O—O— link :

$$H_2SO_5 \qquad H_2S_2O_8$$

Permonosulphuric acid Perdisulphuric acid

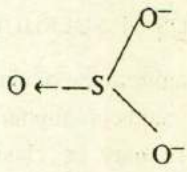
(I) Sulphurous acid, H_2SO_3 : Sulphur dioxide gas dissolves in water to the extent of about 10% by weight at 20°C at the ordinary condition. The solution contains H_2SO_3 :

On cooling a saturated solution of H_2SO_3, crystals have been obtained supposed to contain H_2SO_3 in the hydrated form ($H_2SO_3.6H_2O$).

H_2SO_3 solution is slowly oxidized by oxygen form the air :

$$2H_2SO_3 + O_2 = 2H_2SO_4$$

H_2SO_3 in aqueous solution ionizes to give HSO_3^- and SO_3^{-2} ions ($Ka_1 = 1.3 \times 10^{-2}$, $Ka_2 = 5.6 \times 10^{-8}$). The SO^{-2} ion has a pyramidal structure as the ClO_3^- ion with possible resonance :



Since both HSO_3^- and SO_3^{-2} ions are present, both normal and bisulphite salts are formed from H_2SO_3. This is done by passing appropriate amounts of SO_2 gas into an aqueous solution of the metal carbonates or hydroxides :

$$Ca(OH)_2 + 2SO_2 + H_2O = Ca(HSO_3)_2 + H_2O$$

$$K_2CO_3 + 2SO_2 + 2H_2O = 2KHSO_3 + CO_2 + H_2O$$

$$2NaOH + SO_2 + H_2O = Na_2SO_3 + 2H_2O$$

On heating a bisulphite salt, both water and SO_2 are evolved forming sulphite compound :

$$2NaHSO_3 = Na_2SO_3 + SO_2 + H_2O$$

Further heating of Na_2SO_3 gives rise to an auto-oxidation reduction reaction:

$$4\,Na_2\overset{+4}{S}O_3 = Na_2\overset{-2}{S} + 3Na_2\overset{+6}{S}O_4$$

H_2SO_3 solution is a good reducing agent towards strong oxidizing agents. Thus Cl_2, $KMnO_4$, $K_2Cr_2O_7$ etc. in aqueous solutions oxidize H_2SO_3 to H_2SO_4.

Uses of H_2SO_3 and its salts : (1) Bleaching agent : (2) antiseptic : (3) $Ca(HSO_3)_2$, calcium bisulphite, is extensively used for the manufacture of paper from wood. The chips of wood are digested in $Ca(HSO_3)_2$ solution at 177°C under pressure, as a result the lignin of wood is removed and at the same time the wood pulp is bleached. (4) Na_2SO_3 is used for making other compounds.

Sulphuric Acid

Sulphuric acid is a strong aid generally called "the king of chemicals". Many other chemical industries are based on H_2SO_4 as the basic material. For instance, petroleum refining, fertilizers, paints, drugs, explosives etc. are some of the fields of applications.

The two methods of manufacture of H_2SO_4 are well-known as—(i) Contact Process and (ii) Lead Chamber Process. Both the processes depend upon the oxidation of SO_2 to SO_3.

The Contact Process : Pure sulphur is burnt in air to form SO_2 :

$$S + O_2 = SO_2$$

SO_2 is oxidized by means of air (O_2) in Presence of suitable catalyst (such as Pt, V_2O_5, Fe_2O_3, CuO etc.):

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45 \text{ Kcal}$$

The purity of SO_2 and air is a very important factor. Presence of impurities renders the catalyst ineffective and it is said to be poisoned.

The reversible reaction is exothermic. hence, low temperature favours the formation of SO_3, but the rate of reaction at low temperature is slow. Therefore, in order to increase the rate of reaction the temperature is increased to about 650°C. The temperature is brought down to 450°C while the mixture of SO_2 and air continued to pass. The increased rate of reaction at 650°C and the change of condition to 450°C shift the equilibrium towards the right giving greater yield of SO_3.

Because SO_3 vapour mixed with oxygen does not readily dissolve in water, the SO_3 vapour is passed into a solution of 98% H_2SO_4 in which SO_3 is absorbed smoothly giving pyrosulphuric acid :

$$H_2SO_4 + SO_3 = H_2S_2O_7$$

Water is carefully added to the resulting solution to convert the $H_2S_2O_7$ to H_2SO_4 :

H_2SO_4 made by the Contact Process is quite pure and concentrated.

The Lead Chamber Process : The process derived its name from the fact that the reaction of SO_2 with O_2 in the presence of NO is carried out in large lead-lined chambers. The mode of oxidation of SO_2 to SO_3 is different in this case.

SO_2 may be produced from burning the sulphur or by roasting pyrites or sulphides, such as FeS_2. ZnS etc., SO_2 gas is passed into the lead chamber along with air (O_2), NO, NO_2 and steam. Reactions in the lead chamber are quite complicated but the changes may be represented by the equations :

$$2NO + O_2 \rightleftharpoons 2NO_2$$

$$2SO_2 + 3NO_2 + H_2O \rightleftharpoons \underset{\text{Nitrosyl sulphonic acid}}{2NO(HSO_4)} + NO$$

$$2NO(HSO_4) + H_2O \rightleftharpoons 2H_2SO_4 + NO + NO_2$$

The mixture of NO and NO_2 is recirculated and thus functions as oxygen carrier.

The acid from the Chamber Process contains only 60—70% H_2SO_4. A schematic diagram of the manufacture of H_2SO_4 by the Lead Chamber Process is given in Fig. 21—3.

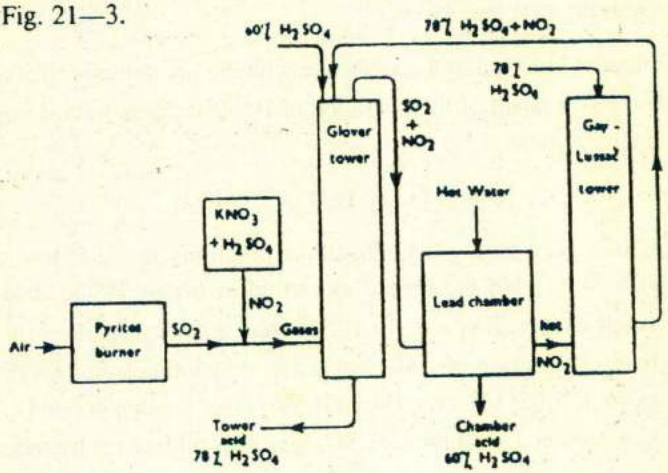


Fig. 21—3. A schematic diagram of the manufacture of H_2SO_4 by the Lead Chamber Process.

Concentration of H_2SO_4 may be increased to 93% by heating in silica or duriron pans (pans made of an alloy of Fe and Si). This may be concentrated by passing hot air from below while the dilute acid is percolated from the top as in the Gaillard Process. Acid made by the Lead Chamber process contains Pb, Fe, As etc.

H_2SO_4 from gypsum : Instead of metal sulphides or sulphur, gypsum, $CaSO_4$, has also been used to produce SO_2. A mixture of $CaSO_4$, SiO_2, clay and coke is heated in a furnace to produce a mixture of gases containing SO_2, N_2 and oxygen known as burner gases :

$$CaSO_4 + 2C = CaS + 2CO_2$$

$$CaSO_4 + CaS + O_2 = 2CaO + 2SO_2$$

$$2CaS + 2CaO + 6SiO_2 + 3O_2 = 6CaSiO_3 + 2SO_2$$

$$2CaS + 2CaO + 2Al_2O_3 + 3O_2 = 6CaO.2Al_2O_3 + 2SO_2$$

This method is specially suitable where gypsum is abundantly available.

Properties of H_2SO_4: 100% pure H_2SO_4 is an oily liquid having covalent bonds. The acid boils at 317°C at which point it has a composition of 98.54% and is reached from either dilute or more concentrated side by loss of SO_3 or H_2O, as the case may be.

Concentrated H_2SO_4 dissolves in water with the liberation of great quantity of heat mostly as a result of the hydration of H^+ ions through the formation of H_2SO_4 as intermediates :

$$H^+ + H_2O = H_3O^+ + 288 \text{ Kcal}$$

H_2SO_4 is a very strong acid. In dilute solutions the first ionization is complete ($Ka_1 \sim 10^3$) but the second ionization involving HSO_4^- takes place only to a small extent ($Ka_2 = 3.5 \times 10^{-2}$). Thus a strong solution of H_2SO_4 contains greater proportion of HSO_4^{-2} whereas very dilute solutions contains a greater proportions of SO_4^{-2} ions. Hence H_2SO_4 gives bisulphates and sulphates of metals. Concentrated solution of H_2SO_4 dissolves all basic substances giving HSO_4^-:

$$H_2SO_4 + NH_3 = NH_4^+ + HSO_4^-$$

$$H_2SO_4 + H_2O = H_3O^+ + HSO_4^-$$

$$H_2SO_4 + KOH = KHSO_4 + H_2O$$

$$Na_2SO_4 + H_2SO_4 = 2NaHSO_4$$

Thus the acid salts may be prepared by the above reactions. Acid salts are highly ionized in aqueous solutions and can be titrated as acid.

Reactions of H_2SO_4: It reacts in three ways :—

(1) ***Oxidizing actions of H_2SO_4***: Dilute H_2SO_4 does not react with metals which occur below hydrogen in the E.M.F. series. Metals above hydrogen react to give H_2 with dilute H_2SO_4. for instance, Zn is oxidized to Zn^{+2} state and H^{+2} is reduced to H_2 in the zero oxidation state :

$$\overset{0}{Zn} + H_2SO_4 = \overset{+2}{Zn}SO_4 + H_2$$

In this type of reaction oxidation state of S is not changed. But when hot and concentrated H_2SO_4 is used, a different types of oxidation-reduction reaction takes place is which S is involved in the reaction and no H_2 is evolved. Thus when hot and concentrated H_2SO_4 is used, the following reactions take place :

$$\overset{0}{Cu} + 2H_2\overset{+6}{S}O_4 = \overset{+2}{Cu}SO_4 + \overset{+4}{S}O_2 + 2H_2O$$

$$\overset{0}{C} + 2H_2\overset{+6}{S}O_4 = \overset{+4}{C}O_2 + 2\overset{+4}{S}O_2 + 2H_2O$$

$$2HI + H_2SO_4 = \overset{0}{I_2} + \overset{+4}{S}O_2 + 2H_2O$$

(2) Dehydrating reactions : When H_2SO_4 is added to water a great deal of heat is evolved because of the formation of H_3O^+ ions. H_2SO_4 has great affinity for water and hence its use as an efficient drying agent for gases and liquids which do not react with it chemically. H_2O may also be removed from some organic substances so effectively that only carbon is left, e. g., from sugar and glucose :

$$C_{12}H_{22}O_{11} + 11H_2SO_4 = 12C + 11(H_2SO_4.H_2O)$$

Formic acid, oxalic acid etc. are converted to CO, CO_2 etc. :

$$HCOOH + H_2SO_4 = CO + H_2SO_4.H_2O$$

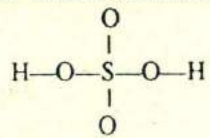
Most organic substances such as cotton, wood etc. are carbonized by concentrated H_2SO_4 for the same reason.

(3) Displacement of compounds due to high boiling point : Volatile acids, such as HCl, HNO_3 etc., are readily displaced by the reaction of their respective salts with concentrated H_2SO_4. H_2SO_4 being non-volatile is left behind if present in excess :

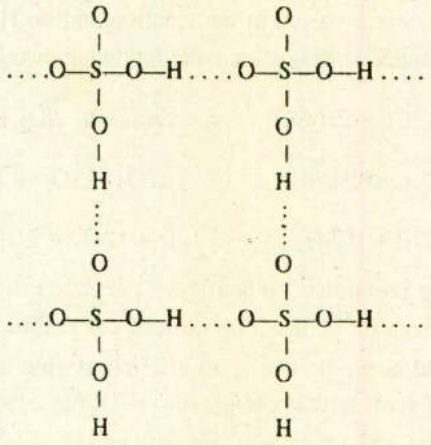
$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

$$KNO_3 + KHSO_4 = KHSO_4 + HNO_3$$

Structure of H_2SO_4 : The S atom in SO_4^{+2} is surrounded tetrahedrally by the four oxygen atoms. The H atoms form hydrogen bonds between these SO_4 tetrahedra in three-dimensional pattern and hence the boiling



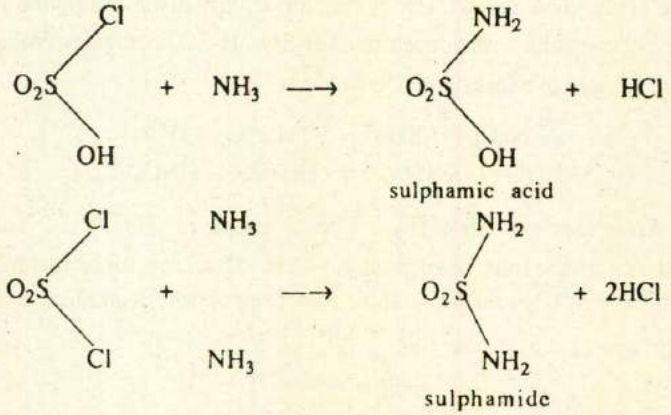
point (or decomposition temperature) of H_2SO_4 is very high. A two-dimensional pattern is given below :



Derivatives of H_2SO_4

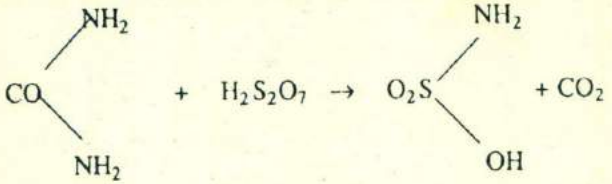
(1) Mono-acid chloride and di-acid chloride of H_2SO_4 have already been described. These are also known as chlorosulphonic acid $Cl.SO_2.OH$ and sulphuryl chloride, $ClSO_2.Cl$, respectively.

(2) Chlorosulphonic acid or sulphuryl chloride, on treatment with NH_3, gives the corresponding amides known as *sulphamic* acid and *Sulphamide* respectively.



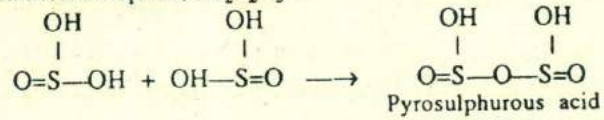
Sulphamic acid HSO_3NH_2 is an stable solid and is used as a primary standard for alkali titrations. ammonium sulphamate, $NH_4SO_2.NH_2$, has been used as a weed-killer and as fire-proofing agent.

Sulphamic acid can also be prepared from urea and fuming H_2SO_4 :



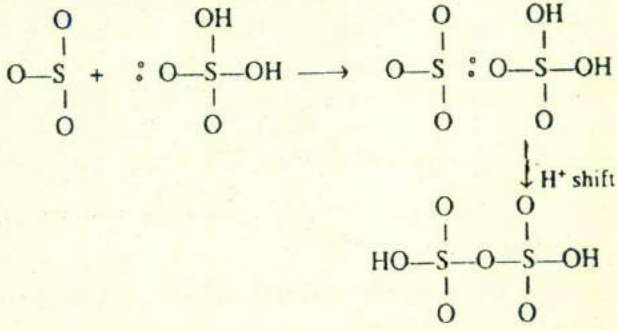
(3) Metal sulphates tend to hold one molecule of water (anion water) by H bond as in the case of $CuSO_4.5H_2O$, i.e., $[Cu(H_2O)_4]^{+2}\,[SO_4 \cdot H_2O]^{-2}$ All other hydrated sulphates can be represented in the same manner. Large number of double sulphates of many metals (alums) are formed.

Pyroacids of sulphur : These have been mentioned earlier. Both pyrosulphurous acids and pyrosulphuric acids are known. Pyrosulphurous acid, $H_2S_2O_5$, is formed by heating a bisulphite and by acidification. SO_2 may be absorbed by H_2SO_3 to give $H_2S_2O_5$. The sodium salt is incorrectly known as sodium metabisulphite, $Na_2S_2O_5$:



Pyrosulphurous acid

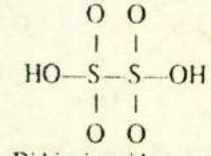
SO_3 is absorbed by concentrated H_2SO_4 to give a number of pyro-acids, $H_2S_2O_7$, $H_2S_3O_{10}$ and $H_2S_4O_{13}$. These are present in oleum. The reaction between SO_3 and H_2SO_4 may be represented as :

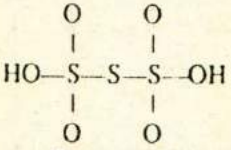


Pyrosulphuric acid

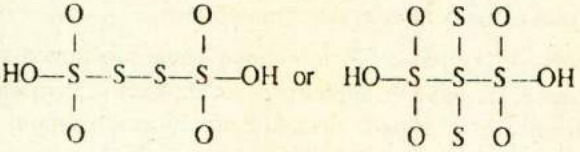
Thioacids of Sulphur

(a) Thionic acids : These consist of the general formula H_2SxO_6 where x can vary from 2 to 6. Obviously, it is the S—S bond which is responsible for the various thionic acids. In fact, these are analogous to the peroxy acids containing O—O chain :


Dithionic acid


Trithionic acid

Tetrathionic acid is formulated in two forms :



The acids have never been isolated, but salts of each acid have been made.

Dithionic acid, $H_2S_2O_6$, is a strong acid and is not oxidized by even $KMnO_4$, Cl_2. $Na_2S_2O_6$ is prepared by the oxidation of SO_2 or Na_2SO_3 either by electrolytic method or MnO_2 :

$$2NaHSO_3 + MnO_2 \rightarrow Na_2S_2O_6 + Mn(OH)_2$$

The other thionates are made by reduction of H_2SO_3 or $NaHSO_3$ by electrolytic process. The tetrathionate, e.g., $Na_2S_4O_6$, is most easily made by the action of I_2 on sodium thiosulphate, $Na_2S_2O_3$, or by the anodic oxidation of $NaHS_2O_3$:

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

$$NaHS_2O_3 \xrightarrow[\text{oxidation}]{\text{anodic}} Na_2S_4O_6$$

Salts of thionic acids are water-soluble, unstable and are decomposed by alkali to sulphites and thiosulphates.

(b) Thionous or hyposulphurous acid, $H_2S_2O_4$: The salt $Na_2S_2O_4$ is known as sodium dithionite, sodium hydrosulphite or hypo-sulphite. This is made by reducing Na_2SO_3 or Na_2HSO_3 with zinc in alcohol or by cathodic reduction of HSO_3^- ions :

$$2NaHSO_3 + Zn + SO_2 = Na_2S_2O_4 + ZnSO_3 + H_2O$$

$$2NaHSO_3 \xrightarrow[\text{reduction}]{\text{cathodic}} Na_2S_2O_4 + H_2O$$

$Na_2S_2O_4$ is a powerful reducing agent and is used in industry as a bleach for dyes, such as indigo blue to indigo white. Cu_2H_2 and CuH_2 are formed with $CuSO_4$. Air oxidizes it to $Na_2S_2O_5$.

(c) Thiosulphuric acid, $H_2S_2O_3$

Sodium thiosulphate : Sodium thiosulphate, $Na_2S_2O_3$, is a common reagent in the laboratory and is known as hypo in photography. It is obtained commercially as $Na_2S_2O_3.5H_2O$ by the following methods :—

(i) Boiling Na_2SO_3 solution with sulphur powder, the solution is filtered and crystals of $Na_2S_2O_3$ separated by evaporation :

$$Na_2SO_3 + S = Na_2S_2O_3$$

(ii) Adding I_2 to a mixture of Na_2S and Na_2SO_3 :

$$Na_2S + Na_2SO_3 + I_2 = 2NaI + Na_2S_2O_3$$

(iii) $Na_2S_2O_3$ is manufactured from Na_2S, Na_2CO_3 and SO_2 :

$$2Na_2S + Na_2CO_3 + 4SO_2 = 3Na_2S_2O_3 + CO_2$$

(iv) Also by the reaction of Na_2CO_3 and SO_2 and sulphur :

$$Na_2CO_3 + H_2O + 2SO_2 = 2NaHSO_3 + CO_2$$

$$2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + H_2O + CO_2$$

$$Na_2SO_3 + S = Na_2S_2O_3$$

In each case the solution after filtration is evaporated and $Na_2S_2O_3.5H_2O$ is isolated by crystallisation.

Properties and uses : $Na_2S_2O_3.5H_2O$ (hypo) is a colourless crystalline substance. It is a good reducing agent and is used in the photographic processing known as fixing which dissolves the excess AgBr not reduced to metallic silver by the developer :

$$AgBr + Na_2S_2O_3 = NaAg(S_2O_3) + NaBr$$

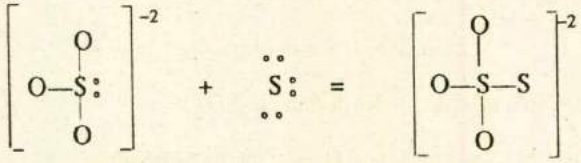
With I_2 it gives $Na_2S_4O_6$:

$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

This reaction is quantitative and is the basis of most iodometric and iodimetric methods of analysis, e.g., in the determination of Cu^{+2}. The formation of $S_4O_6^{-2}$ ions occurs only with weak oxidizing agent, such as I_2. Strong oxidizing agent converts the $S_4O_6^-$ ions to SO_4^{-2} ions.

$Na_2S_2O_3$ is also used to remove excess chlorine in the bleaching industry. for this reason sodium thiosulphate is also known as *antichlor*.

Structure : $S_2O_3^{-2}$ ion is similar in structure to SO_4^{-2} ion. The mode of preparation from SO_3^{-2} and S itself is indicative of the structure :



This $S_2O_3^{-2}$ ion is, in fact, SO_4^{-2} ion in which one oxygen atom has been replaced by the sulphur atom. In $S_2O_3^{-2}$ ion the central S atom has oxidation number –2. The average oxidation number of S in $S_2O_3^{-2}$ ion is +2. The two S atoms are, therefore, non-equivalent. There is no transfer or exchange of S atoms in $S_2O_3^{-2}$ ion.

When $Na_2S_2O_3$ is treated with a dilute solution of a strong acid, $H_2S_2O_3$ formed in solution is readily decomposed to give elementary S and SO_2 :

$$Na_2S_2O_3 + 2H^+ \rightarrow 2Na^+ + S^- + H_2SO_3$$

$$\downarrow\uparrow$$

$$SO_2 + H_2O$$

Peroxysulphuric acids : Two important acids containing —O—O— link are known. These are :

Permonosulphuric acid (Caro's acid)—H_2SO_5

Perdisulphuric acid (Marshall's acid)—$H_2S_2O_8$

$H_2S_2O_8$ is obtained by various methods :—

(a) S_2O_7 formed in small amounts by an electric discharge in a mixture of SO_2 and O_2 dissolves in water to give $H_2S_2O_8$.

(b) Action of cold concentrated H_2SO_4 and concentrated H_2O_2 gives $H_2S_2O_8$:

$$2H_2SO_4 + H_2O_2 = H_2S_2O_8 + 2H_2O$$

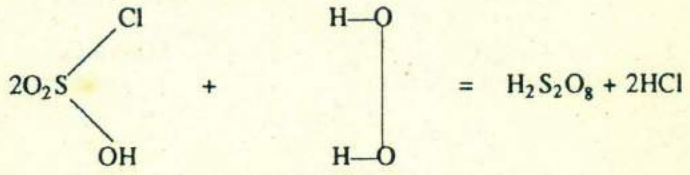
(c) Anodic oxidation of H_2SO_4. (60% solution) gives $H_2S_2O_8$ (see page .....):

$$2HSO_2^- - 2e \rightarrow H_2S_2O_8$$

Concentrated H_2SO_4 is electrolysed in a cell having Pt anode separated from the copper cathode coiled round the outer cylinder.

If concentrated solution of $(NH_4)_2SO_4$ or K_2SO_4 dissolved in concentrated H_2SO_4 is used as the electrolyte, crystals of $(NH_4)_2S_2O_8$ or $K_2S_2O_8$ separate out at the anode compartment.

(d) Pure $H_2S_2O_8$ in the anhydrous state is made by the reaction of chlorosulphonic acid with pure H_2O_2 :



$H_2S_2O_8$ is a very hygroscopic crystalline substance, melts at 65°C and decomposes with loss of oxygen. It is hydrolysed easily giving first H_2SO_5 and then H_2O_2 and is used for the technical production of H_2O_2. The acid and its

salts are powerful oxidizing agents. In alkaline solutions Ag, Ni, Co, Pb etc. are converted to their peroxides :

$$2AgNO_3 + K_2S_2O_8 + 2H_2O = 2KHSO_4 + 2HNO_3 = Ag_2O_2$$

$K_2S_2O_8$ oxidizes Fe^{+2} to Fe^{+3}, Cr^{+2} to Cr^{+3} and to CrO_4^{-2} and even I_2 to IO_3^-. But it does not decolourize $KMnO_4$ solutions.

Caro's acid, H_2SO_5 : It is obtained from $K_2S_2O_8$ by the action of H_2SO_4 at low temperature and controlled hydrolysis with ice :

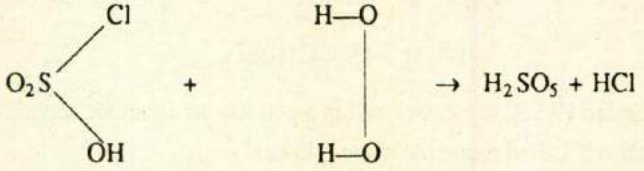
$$K_2S_2O_8 + H_2SO_4 = H_2S_2O_8 + H_2SO_4$$

$$H_2S_2O_8 + H_2O = K_2SO_5 + H_2SO_4$$

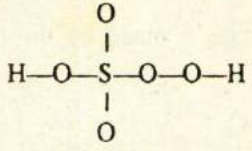
When SO_3 reacts with H_2O_2, Caro's acid is formed :

$$SO_3 + H_2O_2 = K_2SO_5$$

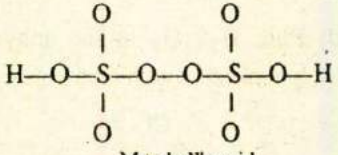
It is also obtained when $ClSO_3H$ is reacted with proper quantity of H_2O_2 :



H_2SO_5 is also readily hydrolysed to give H_2O_2 and H_2SO_4. In fact, these acids are derivatives of H_2O_2 containing —O—O— linkages and H atoms replaced by HSO_3 group one by one :



Caro's acid
(Permonosulphuric acid)



Marshall's acid
(Perdisulphuric acid)

CHROMIUM, MOLYBDENUM AND TUNGSTEN

(The Elements of Group VIB)

The elements of sb-group VIB, Cr, Mo and W are transition metals. Uranium used to be included in this group, but U now belongs to the Actinide

series of elements and hence it is excluded from this group. In the present book the individual chemistry of chromium will only be described.

Although Cr, Mo and W (Wolfram) have some similarities with the elements of group VIA, O, S, Se and Te, the marked difference between sub-group VIA and VIB arises due to the electronic configurations.

Comparison between S and Cr groups :

(a) Similarities : There is no resemblance in the various elements of the group except in certain compounds, such as,

(1) Both the sub-groups exhibit the highest oxidation state of +6 in many compounds, e.g., H_2SO_4, H_2CrO_4 etc.

(2) The compounds, CrO_3, MoO_3 and WO_3 are highly acidic as is SO_3 and with water produce the respective acids:

(3) SO_4^{-2} and SeO_4^{-2} compounds are isomorphous with CrO_4^{-2} and MoO_4^{-2} compounds and show similar behaviour.

(4) H_2CrO_4 and H_2MoO_4 have similar acid behavior as H_2SO_4 and H_2ScO_4.

(5) $BaCrO_4$ is as insoluble as $BaSO_4$. Similarly, $PbSO_4$ and $PbCrO_4$ are insoluble compounds.

(6) CrO_2Cl_2 behave like SO_2Cl_2 in some properties and particularly in easy hydrolysis.

(b) Dissimilarities : The points of dissimilarities can be best understood from the electronic configurations. In the case of Sulphur Family the outer electron levels have the arrangement of s^2p^4, but the arrangements in Cr, Mo and W as,

S (16)—Ne core, $3s^23p^4$

Cr (24)—Ar core, $3d^54s^1$

Mo (42)—Kr core, $4d^55s^1$

W (74)—Xe core, $4f^{14}\ 5d^46s^2$

The outer electron orbitals in the case of Cr, Mo and W consist of $3d^5 4s^1$, $4d^5 5s^1$, and $5d^4 6s^2$ respectively although the total of 6 valence electrons are present in each sub-group. The presence of incomplete **d** orbitals in Cr, Mo and W makes their chemistry very different from those of the S group.

Some of the points of contrasts may be enumerated as follows :—

1. Chromium group elements are transition metals with high density. Sulphur group elements are mostly non-metals, only tellurium shows metallic property.

2. Chromium group metals occur only in the combined state and are extracted from their ores with difficulty. Sulphur group elements occur free in nature and also as compounds.

4. Lower oxides of chromium group elements are basic or amphoteric. Thus CrO is basic and Cr_2O_3 is amphoteric. But lower oxides of sulphur group are acidic. Thus SO_2, SeO_2 are acidic.

5. Chromium group elements show a large number of variable oxidation states than sulphur group and form coloured compounds. $K_2Cr_2O_7$, $KCrO_2$ and K_2CrO_4 are coloured.

6. Chromium group elements do not combine with hydrogen to form volatile hydrides. But H_2S, H_2O, H_2Se are very well-known compounds.

7. Three is a marked tendency for the formation of more complex ployacid compounds in the case of chromium (and particularly Mo). Ammonium phosphomolybdate $(NH_4)_3[PMo_{12}O_{40}]$ is a well-known example.

8. Chromium group elements, because of the unfilled **d** orbitals, form a very large number of complex compounds which is not so well-marked in the sulphur group.

$Cr(NH_3)_6Cl_3$, $Cr(H_2O)_6Cl_3$ etc. are Cr-complexes; but no such compounds are formed with sulphur.

Chromium in some of its properties resembles Mn and Fe which are in group VII and VIII. The metallic property, oxidation states, oxidizing and magnetic properties of some salts of Cr, Fe and Mn appear to be alike because these ar 3d transition metals.

Group Properties of Cr, Mo and W

(a) Physical properties : Some of the physical properties of Cr, Mo and W are given in Table 21·4.

Table 21.4. Physical properties of Cr, Mo and W.

Element	*Cr*	*Mo*	*W*
At. No	24	42	74
At. Wt.	52.01	95.95	183.92
Outer electron orbitals	$3d^5 4s^1$	$4d^5 5s^1$	$5d^4 6s^2$
Ionization potential (ev)	6.74	7.35	7.98
Atomic radius (Å)	1.25	1.36	1.37
Ionic radius			
Ion M^{+6} (Å)	0.52	0.62	0.68
Melting point (°C)	1575	2620	3370
Boiling point (°C)	2475	4800	5930
Oxidation potential (v)	Cr/Cr^{+2} 0.91	Mo/Mo^{+3} 0.20	W/W^{+2} 0.04
Electronegativity	1.56	1.30	1.40

Table 21.5. Reactions of Cr, Mo and W.

Reaction with	*Cr*	*Mo*	*W*	*Conditions*
Air (O_2)	Cr_2O_3	MoO_3	WO_3	On strong heating
F_2	CrF_3	MoF_6	WF_6	On heating
Cl_2	$CrCl_3$	$MoCl_6$	WCl_6	"
Br_2	$CrBr_3$	$MoBr_4$	WBr_6	"
Acids (HCl, H_2SO_4)	Cr^{+2}, Cr^{+3}	No reaction	No reaction	
HNO_3	Cr^{+3} Soln.	MoO_3 ppt.	WO_3 ppt.	Boiling
Alkali	CrO_2^- (Soln.)	No reaction	WO_4^{-2} (soln.)	Boiling
Carbon	Cr_2C_3 interstitial	WC Refractory	MoC Refractory	High temperature
N_2	CrN (hydrolysed)	No action	No action	On strong heating
S	CrS	MoS_2	WS_2	On heating
H_2	No reaction	No action	No action	Adsorption
Important uses	Special steels	Special steels	Filaments	

(b) Chemical properties : The valence electrons of Cr, Mo and W throw some light on the pattern of chemical properties which are exhibited by these transition metals. The reaction of these metals with familiar reagents do not follow any trend but are varied in nature. Instead of describing reactions in details, these are summarised in Table 21.5 for ready reference.

CHROMIUM

Sources of chromium : Chromium does not occur free in nature. The most important sources are :

Chromite, Chrome iron stone—$FeO.Cr_2O_3$ or $FeCr_2O_4$

Crocoite, Lead chromate—$PbCrO_4$

Chrome ochre—Cr_2O_3

Chromite is the only important ore which is profitably utilized for obtaining chromium and all its compounds.

Metallurgy of Chromium

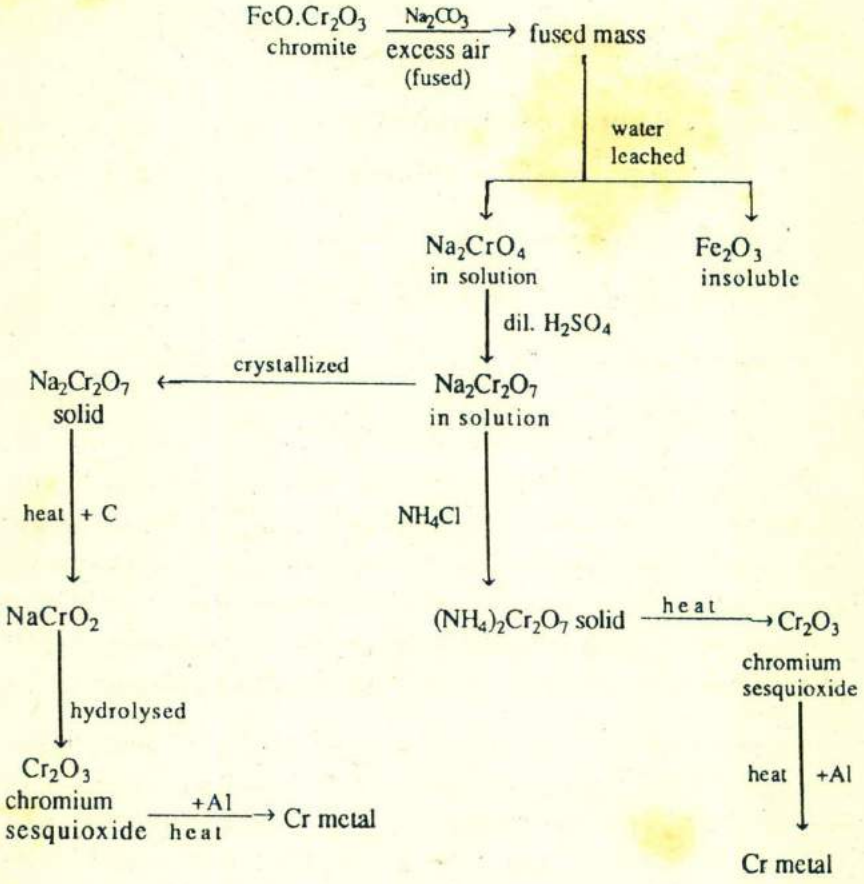
Metallic chromium is normally extracted from chromite or chrome iron ore, $FeO.Cr_2O_3$. The extraction of chromium from chromite depends upon the use for which it is intended.

Ferrochrome : Chromium for steel industry is generally converted to *Ferrochrome*. The crushed chromite ore is freed from the gangue by washing with a current of water. The heavy chromite ore is left behind while the impurities are washed away. The concentrated chromite is then reduced by means of carbon in an electric furnace to give ferrochrome :

Thus Cr_2O_3 can be obtained from $Na_2Cr_2O_7$ by either methods through $NaCrO_2$ or through $(NH_4)_2Cr_2O_7$ as given in the flow sheets on page 601. If K_2CO_3 is used instead of Na_2CO_3, the product formed is $K_2Cr_2O_7$ which can be treated in similar manner to get Cr_2O_3.

Chromium metal is obtained from Cr_2O_3 by aluminothermic process. Cr_2O_3 is mixed with Al powder in a crucible and ignited by means of Mg ribbon and BaO_2 powder. The high thermal energy reduces Cr_2O_3 to Cr :

$$Cr_2O_3 + Al \rightarrow Al_2O_3 + 2Cr + 112 \text{ Kcal}$$



The reactions involved in the fusion process of chromite are given by the following equations :—

1. Fusion :

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 = 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$$

2. Dichromate conversion :

$$2Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

3. (a) Reduction :

$$Na_2Cr_2O_7 + 3C = 2NaCrO_2 + 3CO$$

(b) Hydrolysis :

$$2NaCrO_2 + H_2O = 2NaOH + Cr_2O_3$$

4. (a) Ammonium dichromate conversion :

$$Na_2Cr_2O_7 + 2NH_4Cl = (NH_4)_2Cr_2O_7 + 2NaCl$$

(b) Thermal decomposition :

$$(NH_4)_2Cr_2O_7 \xrightarrow{heat} N_2 + 4H_2O + Cr_2O_3$$

5. Extraction of Cr :

$$Cr_2O_3 + Al \rightarrow Al_2O_3 + Cr$$

Properties of Cr : Chromium is a silvery white and hard metal and has high resistance to corrosion. Its lustre is like platinum and remains untarnished. For this reason, chromium is much used in producing chrome-plated copper and iron materials for motor cars and domestic use. In fact, chromium metal is not very much extracted from chromite but converted to either ferrochrome for steel industry and to chromium compounds for chrome-plating and other purposes.

Chrome plating : This is, in fact, a process for the production of chromium metal by the electrolytic reduction of chromium compounds from aqueous solution. For this purpose, solutions of H_2CrO_4 together with $Cr_2(SO_4)_3$ or other salts, such as borate and phosphate, are added to the electrolytic bath. Very small amount of $Cr_2(SO_4)_3$ is needed. The mixed solutions constitute the electrolytic bath. High current density is used. the article to be plated is the cathode and lead (Pb) is the anode.

Chromium is a rather difficult metal to use as a plating element and the coating tends to fall away due to the porosity. For this purpose, the article to be chrome-plated is given a very thin coating of copper or nicked first and then chrome-plated giving the bright platinum-like appearance on polishing which is not stained even in rain water :

$$CrO_4^{-2} + 8H_3O^+ + 6e \rightarrow Cr^{+3} + 12H_2O$$

$$Cr^{+3} + 3e \rightarrow Cr \text{ (metal)}$$

$$CrO_4^{-2} + 8H_3O^+ + 9e \rightarrow Cr + 12H_2O$$

Thus the real plating agent is Cr^{+3} ion. But the actual concentration of Cr^{+3} ion in the plating bath is kept very small because under this condition the formation of hard deposit of chromium metal takes place.

Although chromium metal is more electropositive than iron and reacts with dilute acids to evolve hydrogen, yet it acquires a firmly held thin film of oxide coating which renders it chemically inactive and it is said to be in the passive state. Chromium exhibits greater passivity than any other metal. Passivity is produced by the action of concentrated HNO_3, H_2CrO_4 or exposure of the metal to air.

Uses of Chromium : (i) In making chrome steel, these are very hard and tough and contain various proportions of chromium.

(ii) Stainless steel : Stainless steel : 12—14% Cr, 0.3%C and rest iron, does not rust and is used in making cutlery, turbine blades, valves etc.

(iii) Nichrome (Chromel) : 60% Ni, 15% Cr and 25% Fe, is used as a resistance wire in heaters and in electric furnace since it is not oxidized at high temperature by air.

Some Important Compounds of Chromium

Chromium is a transition metal with $3d^5 4s^1$ valence electrons and chromium compounds can have several oxidation states. The compounds with +2, +3 and +6 oxidation states are the most common. Compounds with +3 state are very stable, those with +6 state are good oxidizing agents and compounds with +2 state are good reducing agents.

Compounds of Cr of +2 oxidation states : Cr (II) compounds : Chromium metal is electropositive and in the finely divided state dissolves in acids evolving H_2 :

$$Cr + 2HCl = CrCl_2 + H_2$$

$$Cr + H_2SO_4 = CrSO_4 + H_2$$

Cr(II)halides : These can be obtained by the following methods :—

(1) $Cr \text{ metal} + Cl_2 \xrightarrow{\text{(ignited)}} CrCl_2$ anhydrous chromous chloride

(2) $CrCl_3 + H_2 \xrightarrow[+HCl]{Zn} CrCl_2 + HCl$

(3) $CrCl_2 + HF \rightarrow CrF_2 + HCl$

(4) $Cr + I_2 = CrI_2$ in preference to CrI_3.

Anhydrous $CrCl_2$ is colourless but its solution in water has the bright blue colour of the hydrated $Cr(H_2O)_6^{+2}$ ion. This is unstable and easily oxidized to the hydrated $Cr(H_2O)_6^{+3}$ by aerial oxidation.

Chromous sulphate, $CrSO_4.7H_2O$, prepared by dissolving the metal in H_2SO_4, is isomorphous with $FeSO_4.7H_2O$ and also forms alum, $K_2SO_4.CrSO_4.6H_2O$.

Chromous acetate, $Cr(CH_3COO)_2$: This is prepared in the form of a red precipitate when a saturated solution of sodium acetate is added to a solution of $CrCl_2$ in presence of H_2 :

$$CrCl_2 + 2CH_3COONa = Cr(CH_3COO)_2 + 2NaCl$$

Chromous acetate is insoluble in water and very stable. In general, acetates are soluble but chromous acetate is an exception.

Chromous hydroxide, $Cr(OH)_2$: This is obtained as a brownish-yellow precipitate when NaOH is added to $CrCl_2$ solution :

$$CrCl_2 + 2NaOH = Cr(OH)_2 + 2NaCl$$

$Cr(OH)_2$ is readily oxidized by air to the green $Cr(OH)_3$, much faster than $Fe(OH)_2$.

Cr^{+2} forms relatively few complexes. Solutions of Cr^{+2} are the strongest reducing positive ions in aqueous media, Cr^{+2} forms stable complexes with NH_3 and CN^- as in

$$[Cr(NH_3)_6]Cl_2 \text{ and } K_4[Cr(CN)_6]$$

Chromium(III)compounds : Compounds of Cr of +3 oxidation states : This is the most stable oxidation state of chromium and a number of intensely coloured hydrated salts of trivalent chromium are well-known. The aqueous solution invariably contains the $Cr(H_2O)_6^{+3}$ ion which is violet but the Cr^{+3} salt solutions are often green due to the exchange of H_2O with anion present in the Cr-compounds.

$$[Cr(H_2O)_6]^{+3}Cl_3 \xrightarrow[heat]{H_2O} [Cr(H_2O)_5Cl]^{+2}Cl_2 + H_2O$$

Cr (III) oxide, Cr_2O_3 : Chromium sesquioxide is the middle member of the series of this oxides of Cr, namely CrO (basic), Cr_2O_3 (amphoteric) and CrO_3 (acidic) having Cr in +2, +3 and +6 oxidation states.

Cr_2O_3 is obtained by various methods :—

$$(NH_4)_2Cr_2O_7 \xrightarrow{heat} Cr_2O_3 + N_2 + 4H_2O$$

$$Na_2Cr_2O_7 + S \xrightarrow{heat} Na_2SO_4 + Cr_2O_3$$

$$2NaCrO_2 + H_2O \xrightarrow{boil} Cr_2O_3 + 2NaOH$$

$$Na_2Cr_2O_7 + NH_4Cl \xrightarrow{heat} Cr_2O_3 + N_2 + 4H_2O + 2NaCl$$

Cr_2O_3 may also be obtained by heating $Cr(OH)_3$ precipitate obtained by adding alkali to a Cr^{+3} salt solution :

$$2Cr(OH)_3 \rightarrow Cr_2O_3 + 3H_2O$$

Cr_2O_3 has a beautiful green colour, insoluble and inert and is used as a pigment under the name *Chrome Green*. Cr_2O_3 may be obtained from the mineral chromite already described before.

Chromic hydroxide, $Cr(OH)_3$: When a Cr^{+3} salt solution is treated with alkali hydroxides, carbonate or a solution of sodium or ammonium sulphide, a blue-green precipitate is formed which is $Cr(OH)_3$ but is hydrated to various degrees. The gelatinous precipitate is assumed to have the composition $Cr(OH)_3.(H_2O)_3$. This is amphoteric dissolving both in acid and alkali solutions :

$Cr(OH)_3 + 3H^+ \rightarrow Cr^{+3} + 3H_2O$

$Cr(OH)_3 + OH^- \rightarrow Cr(OH)_4^-$ (Chromite ion)

The conversion of $Cr(OH)_3$ precipitate to chromate by alkaline oxidation is a quite familiar process in analysis. $Cr(OH)_3$ is easily converted to CrO_4^{-2} by oxidation with Na_2O_2, NaOH + Br_2, KNO_3 + Na_2CO_3, NaOH + H_2O_2 etc. :

$$Cr_2O_3 + 4KOH \xrightarrow{+O} 2K_2CrO_4 + 2H_2O$$

Chromic chloride, $CrCl_3$: Anhydrous $CrCl_3$ is obtained by the following reactions :—

$$Cr \text{ (metal)} + Cl_2 \xrightarrow{\text{heat}} CrCl_3$$

$$Cr_2O_3 + 3C + 3Cl_2 \xrightarrow{\text{heat}} 2CrCl_3 + 3CO$$

$$4Cr_2O_3 + 3S_2Cl_2 + 9Cl_2 \longrightarrow 8CrCl_3 + 6SO_2$$

Violet crystals of pure $CrCl_3$ are insoluble in water but dissolves in presence of a little $CrCl_2$ or $CuCl_2$. The dilute solutions of $CrCl_3$ in water is violet, but the strong solution is green. The crystals of $CrCl_3.6H_2O$ in the solid form is green. In concentrated solution $[Cr(H_2O)_4Cl_2]^+$ is responsible for the green colour whereas in dilute solutions $[Cr(H_2O)_6]^{+3}$ assumes the violet tinge. This is also true of $Cr_2(SO_4)_3$ solutions.

Chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$: This is obtained by adding K_2SO_4 to a solution of $Cr_2(SO_4)_3$ which is prepared by the action H_2SO_4 on freshly precipitated $Cr(OH)_3$ or hydrated Cr_2O_3.

Chrome alum is manufactured directly from $K_2Cr_2O_7$ by reduction with SO_2 in presence of H_2SO_4 :

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4.Cr_2(SO_4)_3 + H_2O$$

The deep violet crystals separate on evaporation of the solution. The crystals can be grown to a very large sized octahedron. Chrome alum is isomorphous with other alums. The cold solution is violet but on heating it turns green for the reason stated in the property of $Cr(H_2O)_6^{+3}$ ion.

The formula of chrome alum may also be written as $KCr(SO_4)_2.12H_2O$.

It is the most important of the soluble chromium salts. It is used in the tanning of leather, printing of calico, as a mordant in dyeing industry and in water-proofing of fabrics.

$NH_4Cr(SO_4)_2.12H_2O$ ammonium chrome alum, is obtained by using $(NH_4)_2Cr_2O_7$ as the starting material.

Chromium(VI)compounds : Compounds of Cr of +6 oxidation state : In the +6 oxidation state, chromium is usually combined with oxygen.

Chromium trioxide, CrO_3 : It is obtained by adding concentrated H_2SO_4 to a strong solution of $K_2Cr_2O_7$ in the cold. Scarlet coloured needle-shaped crystals, only slightly soluble in the cold acid, separate out :

$$K_2Cr_2O_7 + 2H_2SO_4 = 2CrO_3 + 2KHSO_4 + H_2O$$

CrO_3 is the anhydride of chromic acid, H_2CrO_4, and reacts with water in different proportion forming H_2CrO_4, $H_2Cr_2O_7$, $H_2Cr_3O_{10}$ etc. These acids exist only in solutions :

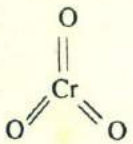
$$CrO_3 + H_2O \rightleftharpoons H_2CrO_4 \rightleftharpoons 2H^+ + CrO_4^{-2}$$

$$2CrO_3 + H_2O \rightleftharpoons H_2Cr_2O_7 \rightleftharpoons 2H^+ + CrO_7^{-2}$$

It is powerful oxidizing agent but does not oxidize CH_3COOH or ether. When heated, it loses oxygen forming the green Cr_2O_3 :

$$4CrO_3 = 2Cr_2O_3 + 3O_2$$

CrO_3 is a covalent compound and melts at 169°C. The structure is given as,



Potassium dichromate, $K_2Cr_2O_7$: It can be directly obtained from chromite ore by fusion with K_2CO_3, and subsequent crystallisation on aqueous

extract. When $Na_2Cr_2O_7$ is produced from chromite, the K-salt is precipitated from $Na_2Cr_2O_7$ by adding KCl :

$$Na_2Cr_2O_7 + 2KCl = K_2Cr_2O_7 + 2NaCl$$

Potassium salt is less soluble than the Na-salt. $Na_2Cr_2O_7$, $K_2Cr_2O_7$ and $(NH_4)_2Cr_2O_7$ obtained from chromite are the starting materials for most of the chromium compounds. $K_2Cr_2O_7$ is an oxidizing agent and is used in quantitative chemical analysis of Fe^{+2}, soluble S^{-2}, SO_2 etc. It is also used in dying and chrome tanning. A mixture of $Na_2Cr_2O_7$ and H_2SO_4 is used in chromic acid mixture as a cleaning solution for glasswares in the laboratory. This is because of the strong oxidizing power of $Cr_2O_7^{-2}$ ion and dehydrating action of concentrated H_2SO_4.

Potassium chromate, K_2CrO_4 : Potassium, K_2CrO_4, or sodium chromate, Na_2CrO_4, may be obtained directly from chromite by the reaction :

$$4FeCrO_4 + 8K_2CO_3 + 7O_2 = 2Fe_2O_3 + 8K_2CrO_4 + 8CO_2$$

The yellow K_2CrO_4 is extracted with water and crystallised. It may be obtained by the following reactions also :

$$2Cr(OH)_3 + 10KOH + 3Br_2 = 2K_2CrO_4 + 6\,KBr + 8H_2O$$

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O$$

When K_2CrO_4 is added to $BaCl_2$, the yellow $BaCrO_4$ is precipitated out. This is used as a pigment under the name *Lemon Chrome*. $AgNO_3$ gives a brick-red precipitate of Ag_2CrO_4. Pb-acetate forms two types of precipitates. $PbCrO_4$ is yellow and is known as *Chrome Yellow*. When $PbCrO_4$ is digested with alkali, it is converted to basic lead chromate, $PbO.PbCrO_4$, which is known as *Chrome Red*. By mixing varying proportions of $PbCrO_4$ and $PbO.PbCrO_4$, another pigment is obtained which is known as *Chrome Orange*.

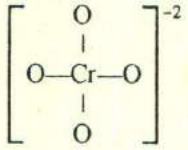
The chromate-dichromate equilibrium : Cr^{+6} generally exist as $Cr_2O_7^{-2}$ ion in aqueous acid solution but in the neutral or alkaline solutions it forms CrO_4^{-2} ion. Thus by adding acid to the yellow CrO_4^{-2} solution, it changes to orange $Cr_2O_7^{-2}$ ion :

$$CrO_4^{-2} + 2H^+ \rightleftharpoons Cr_2O_7^{-2} + H_2O$$

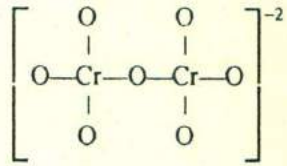
On adding alkali to $Cr_2O_7^{-2}$ ion the orange colour is changed to yellow of CrO_4^{-2} :

$$Cr_2O_7^{-2} + OH^- \rightleftharpoons 2CrO_4^{-2} + H_2O$$

In strong acid solution, further linking of CrO_4^{-2} to more condensed polychromate occurs. The CrO_4^{-2} has similar structure as SO_4^{-2} and in $Cr_2O_7^{-2}$ the atoms are linked through an oxygen atoms as in pyrosulphate :



and



It is to be noted that when Pb-acetate solution is added to $K_2Cr_2O_7$ solution, the precipitate of $PbCrO_4$ is formed rather than $PbCr_2O_7$ because the solubility product of $PbCrO_4$ is much lower than that of $PbCr_2O_7$. The small amount of CrO_4^{-2} in $Cr_2O_7^{-2}$ solution is precipitated out as $PbCrO_4$ shifting the equilibrium toward CrO_4^{-2} ion.

Chromyl chloride, CrO_2Cl_2 : This is analogous to SO_2Cl_2 and contains Cr in the +6 state. This is formed when a metal chloride, such as NaCl is heated with $K_2Cr_2O_7$ and concentrated H_2SO_4.

The deep red vapour of CrO_2Cl_2, which evolves on heating, condenses to a dark-red liquid at the room temperature :

$$K_2Cr_2O_7 + 6H_2SO_4 + 4\,NaCl = 2CrO_2Cl_2 + 2KHSO_4 + 4NaHSO_4 + 2H_2O$$

The vapour of CrO_2Cl_2 is soluble in water by hydrolysis :

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl$$

The aqueous solution gives a precipitate of $PbCrO_4$ with Pb-acetate solution.

Neither bromide nor iodide forms this type of compound and the formation of CrO_2Cl_2 is used as an efficient means to detect the presence of Cl^- either alone or in presence of Br^- and I^- ions.

Peroxychromates : A number of perchromates has been made but the familiar blue ether soluble CrO_5 is obtained by adding H_2O_2 to a solution of $K_2Cr_2O_7$ in presence of H_2SO_4. The peroxychromate gives blue solution extracted by ether. CrO_5 is only a possible composition and $HCrO_5$ has also been proposed for the same substance.

Molybdenum and Tungsten

Molybdenum occurs chiefly as molybdenite, MoS_2. and tungsten as wolframite, $FeWO_4$. Mo and W are obtained from the respective ores by the following processes :

$$MoS_2 \xrightarrow[O_2]{\text{roasting}} MoO_3 \xrightarrow[\text{heat}]{H_2 \text{ or Al}} Mo$$

$$FeWO_4 \xrightarrow{Na_2CO_3} \begin{cases} \rightarrow Fe_2O_3 \text{ insolution} \\ \rightarrow \underset{\text{water soluble}}{Na_2WO_4} \xrightarrow{HCl} WO_3 \xrightarrow[\text{heat}]{C} W \end{cases}$$

The properties of Mo and W are subjected to the dragging effect of lanthanide contraction and the +6 oxidation states are important in both the metals. Both MoO_3 and WO_3 are stable and acidic but less than that of CrO_3. MoO_3 and WO_3 dissolve in alkali to form molybdates and tungstates containing MoO_4^{-2} and WO_4^{-2} ions respectively. The tendency for condensation of molybdate and tungstate ions is far greater than that of chromate and hence ploymolybdates and polytungstates are quite numerous.

Ammonium molybdate, $(NH_4)_2MoO_4$, is formed when MoO_3 is dissolved in NH_4OH and recrystallised. $(NH_4)_2MoO_4$ is the familiar compound used for testing PO_4^{-3} ion. In presence of HNO_3 ammonium mloybdate gives a canary yellow precipitate usually called ammonium phosphomolybdate of the composition $(NH_4)_3PO_4.12MoO_3.H_2O$. Both M and W show variable oxidation states as discussed before, particularly W has +2, +3, +4, +5 and +6 states.

Uses of Mo and W : Molybdenum and tungsten are used to produce special steels and for high speed tools.

QUESTIONS AND PROBLEMS

1. How would you prepare the following compounds ? Give their reactions and tests : (a) Sodium thiosulphate, (b) Sulphonyl chloride.
2. What are persulphuric acids ? How are these prepared ? Describe some important properties of these acids.
3. Write the electronic structure of sulphur chloride.
4. Sketch and explain the flow sheet for the manufacture of sulphuric acid by the Contact Process. Compare the different catalysts used in the process. Also give the advantages of the Contact Process over the Chamber Process.
5. (a) What is chromite ? What are its important uses ?
   (b) Starting with chromite, how would you obtain pure Cr_2O_3.
   (c) Cite some examples of the complex salts of chromium.
6. Describe in detail the various steps involved in the extraction of chromium metal from its ore laying special emphasis on the type of equipments used in the process. Give important uses of this metal.
7. Describe the preparation, properties and uses of the following :—
   (a) Ferrochrome from chromite.
   (b) Sulphur trioxide.
   (c) Sodium thiosulphate.
   (d) Potassium dichromate.
8. Explain the principle underlying the use of hydrogen sulphide in group separation of inorganic qualitative analysis.
9. Compare the chemistry of sulphur and chromium and mention uses of their important compounds.
10. How would you prepare—(a) thionyl chloride from sodium sulphite. (b) lead chrome from lead monoxide (PbO) (c) chromium oxide (Cr_2O_3) from chromite ?
11. Give a brief description of aluminothermic process of chromium.
12. Starting from chrome-iron ore, how would you obtain specimens of the following:—(a) K_2CrO_4 ; (b) CrO_2Cl_2 ; (c) Cr_2O_3 ; (d) $(NH_4)_2Cr_2O_7$ and (e) chrome alum ? Give equations of the reactions involved.
13. Describe the preparation and properties of the following:—(a) chromyl chloride (b) sodium thiosulphate. (c) ferrochrome.
14. Compare the chemistry of the following elements and their compounds :— Oxygen, sulphur, selenium and tellurium. Justify their position in the Periodic Table and give their atomic structure.

15. Describe the preparation, properties and structure of the following : (a) Sulphurous acid, (b) perdisulphuric acid.
16. What is stainless steel ?
17. Starting from chromite how will you get ferrochrome and potassium chromate ? Write he structural formula of CrO_3, $[Cr(H_2O)_6]^{+3}$ and K_2CrO_4.
18. "H_2S is a useful reagent in analytical chemistry" Discuss.
19. Draw and compare the structural formula of H_2SO_4, H_2SO_5, $H_2S_2O_3$, $H_2S_2O_7$ and $H_2S_2O_8$. Name each of these compounds and write at least one chemical equation for each for their preparations.
20. An iron sulphide has been found to have the formula FeSx (x > 1 but not a whole number). Comment on the chemical nature of FeSx.
21. Why do the preparations of H_2SeO_4 and H_2SO_4 follow different processes ?
22. Can you visualize the existence of O_4, keeping in view that both O_3 and SO_3 do exist ?
23. Draw the resonance structures of O_2 and O_3. Do they predict that O_3 should be relatively unstable ? Which rule of resonance may be applied in this case ?
24. Explain : SO_2 is both oxidizing and a reducing agents.
25. Explain : Pure H_2SO_4 conducts electricity whereas pure HCl is a non-conductor.
26. Sulphur shows allotropy whereas this property is not well marked in the case of Se and Te. Explain.
27. SF_6 is well-defined compound but SCl_6 is not known.
28. Explain O—O bond energy in O_2 is much higher than S—S bond energy in S_8. Why ?
29. Compare the properties of H_2O and H_2S.
30. H_2S is a better reducing agent then H_2O. Explain.
31. The normal oxidation states of oxygen is −2 whereas S in the same group of Periodic Table exhibits oxidation states −2, +4 and +6. Discuss.
32. Compare the chemistry of oxygen and sulphur.
33. Discuss the structure of SO_2.
34. Compare the structure of S_2Cl_2, O_2F_2 and H_2O_2.
35. Describe briefly the chemistry of oxyacids of sulphur.
36. The structure of SO_3 in gaseous, liquid and solid state are not the same. Draw the structure.
37. What do you understand by the term "depletion of ozone layer of the atmosphere"? How this is happening ? Describe the effect.
38. Disinfection of drinking water may be brought about by. Cl_2 or O_3. Comment which reagent is preferable for the purpose.

39. Certain quantity of dissolved oxygen in water is necessary for life of aquatic animals. What factors are responsible for the lowering of dissolved oxygen in water and to what adverse effect.
40. Aluminium alum is used for water purification but chromium alum is not. Write the formula and explain why chromium alum can not be used for water treatment.
41. Compare the oxidizing character of $K_2Cr_2O_7$, $K_2S_2O_7$ and $K_2S_2O_8$.

CHAPTER 22

THE HALOGENS AND THE MANGANESE GROUP

(The Elements of Group VII)

The elements of Group VII are divided into two sub-groups VIIA and VIIB. The elements of sub-group VIIA are non-metals and are commonly known as *Halogens*. The sub-group IIB consists of transition metals of which Mn is important. Technetium is radioactive and prepared artificially as it does not occur in nature. Rhenium is rather unfamiliar.

Sub-group VIIA	*Sub-group VIIB*
Halogens	
F — Fluorine	
Cl — Chlorine	Mn — Manganese
Br — Bromine	Tc — Technetium
I — Iodine	Re — Rhenium
At — Astatine	

THE HALOGENS

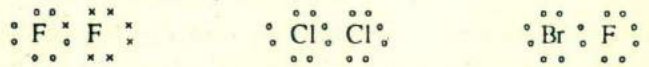
Comparison of the Properties of Halogens

The name halogen was given to the elements of sub-group VIIA because the salts of these elements are common in nature (halogen means salt-former). All these elements combine with alkali metals to produce salt like sodium chloride. The electronic structures of the halogens are given in Table 22.1.

Table 22.1 Electronic structures of the halogens.

At. No.	*Elements*	*Electronic structures*	*Valence electrons*
9	F	(He core) $2s^2\ 2p^5$	$2s^2\ 2p^5$
17	Cl	(Ne core) $2s^2\ 3p^5$	$3s^2\ 3p^5$
35	Br	(Ar core) $3d^{10}\ 4s^2\ 4p^5$	$4s^2\ 4p^5$
53	I	(Kr core) $4d^{10}\ 5s^2\ 5p^5$	$5s^2\ 5p^5$
85	At	(Xe core) $4f^{14}\ 5d^{10}\ 6s^2\ 6p^5$	$6s^2\ 6p^5$

Thus the outermost electron orbitals of F, Cl, Br, I and At consist of s^2p^5 electrons in each case whereas the inert gas outer orbitals contain s^2p^6 electrons. The chemical behaviours of halogens, therefore, show a tendency to achieve the inert gas configuration by accepting an electron from other atoms either by transfer or by sharing. At the ordinary temperatures the halogens exist as diatomic molecules, F_2, Cl_2, Br_2 and I_2 for the same reason, because diatomic halogens have achieved stability by sharing an electron from each atom in an electron pair bond (covalent molecules) :



A list of some of the physical properties are given in Table 22.2 It may be pointed out that these figures are not to be committed to memory but have been included to facilitate the study on the basis of the electronic structures.

The relative sizes of the halogens are particularly useful in explaining many of their physical and chemical properties. The increase in the sizes of the atomic and ionic radii with the increasing atomic number appears to be more well-marked from F to Cl than from Cl to the succeeding halogens. This is an indication that F has a sharp difference in properties as compared to other halogens. The screening electrons in F atom are only two ($1s^2$) followed by the 7 outermost electrons ($2s^2\ 2p^5$). But the other halogens have at least one complete shell of 8 shielding electrons in addition to other shielding levels. Thus the reactivity of F_2, by and large, is the greatest of all halogens. Chlorine and bromine have more chemical similarity because their atomic and ionic radii have

nearly similar values with only slight difference. The incomplete nuclear shielding of 3d electrons in bromine is responsible for this characteristic.

The colours of the halogens (or as a matter of fact any other substance) arise due to absorption of visible light which excites one or more electrons of the outer levels to higher energy levels. The values of the ionization potentials of halogens as given in Table 22.2 indicate this trend. F_2 requires high energy for excitation and hence is pale yellow and the excitation of electrons from I_2 molecule requires lower energy and appears dark violet. From F_2 to I_2 the colour deepens for the same reason.

The melting and boiling points of halogens regularly increase with the increase in their atomic number or molecular weights. As the size of the atoms increases, the electron clouds of the halogen molecules become larger and more readily distorted or polarized.

The greater the size of the electron clouds, the greater is the deformation and elements show greater increase in the van der Waals' forces. Thus at room temperature F_2 is a pale yellow gas, Cl_2 is a greenish yellow gas, Br_2 is a reddish-brown liquid and I_2 is a dark violet solid. Astatine is also a solid having somewhat metallic character. These physical states may be explained on the basis of the relative strengths of the attractive forces acting between the halogen molecules. The diatomic I_2 molecules form the crystal lattice linked together by strong van der Waals' forces among the outermost electrons and hence it is solid. Br_2 is liquid; Cl_2 and F_2 are gases due to decrease in the attractive forces between the molecules (weaker van der Waals' forces) and this trend is indicated by the values of the heats of vaporization of the halogens in Table 22.2

The dissociation energy of halogens indicate that the halogen molecules are quite stable because of the inert gas configuration. Cl_2 molecule is more stable than Br_2 which is more stable than I_2 indicating decrease in the stability of covalent bond with the increase in the size of the atoms.

$$F_2 \rightarrow F + F + 37.8 \text{ Kcal}$$

$$Cl_2 \rightarrow Cl + Cl + 58.0 \text{ Kcal}$$

$$Br_2 \rightarrow Br + Br + 53.4 \text{ Kcal}$$

$$I_2 \rightarrow I + I + 51.0 \text{ Kcal}$$

Table 22.2. Properties of the halogens.

Properties	*F*	*Cl*	*Br*	*I*	*At*
Atomic No.	9	17	35	53	85
Atomic Wt.	19.00	35.46	79.92	126.92	210
Physical state	Pale Yellow gas	Greenish-yellow gas	Reddish-brown liquid	Violet black solid	Solid almost metallic
Outer electron Orbitals	$2s^2\ 2p^5$	$3s^2\ 3p^5$	$3d^{10}4s^2\ 4p^5$	$4d^{10}5s^2$ $5p^5$	$4f^{14}\ 5d^{10}$ $6s^2\ 6p^5$
Covalent radius (Å)	0.72	1.00	1.14	1.35	—
Ionic radius (Å)	1.36	1.81	1.16	2.16	—
Ionization potential (ev)	17.42	13.01	11.84	10.45	9.50
Melting point (°C)	− 223	−102	− 7	114	—
Boiling point (°C)	−188	− 34	59	185	—
Electronegativity	4.00	3.00	2.80	2.50	2.20
Electrode potential X/X	− 2.87	− 2.36	− 1.10	− 0.54	− 0.30
Oxidation states	−1,0	−1,0,1,3 5,7	−1,0,1,3,5	−1,0,1, 5,7	—
Dissociation energy $X_2 \rightleftharpoons 2X$ (Kcal)	37.80	58.00	53.40	51.00	27.70
Electron affinity (ev)	3.70	4.00	3.80	3.40	3.20
Heats of vaporization (Kcal/mole)	1.60	4.40	7.40	10.40	—

In general, the strengths of the covalent bond increase with the decrease in the atomic size. But F_2 is an exception to this rule. The small value of F—F bond energy is possibly due to the repulsion of non-bonding electrons in the small F atom.

The very great oxidizing power of F molecule is associated with the low heat of dissociation and high heat of hydration of the fluoride (F^-) ion and not with the electron affinity of F having about the same value as that of Br_2.

Halogens with high atomic numbers show greater tendency to increase their oxidation numbe as compared to that of F. This trend is best exemplified by the following interhalogen compounds. F combines with only one F, whereas other halogens can combine with 3, 5 and 7 fluorines :

F—F $\quad ClF_3 \quad BrF_5 \quad IF_7$

In the above compounds F has, 7, Cl has 7+3 (=10), Br has 7+5 (=12) and I has 7+7 (=14) total number of valence electrons.

Halides of the same metals, such as SnF_4, $SnCl_4$, $SnBr_4$ and SnI_4 or AgF, AgCl, AgBr and AgI etc. exhibit different bond character. The fluorides are almost ionic whereas the iodides are almost covalent. This is attributed to the electronegativity and the extent of polarization of the halide ions. The crystal structures of the halides also depend upon the electronegativity difference of the metals and the halogens and their polarization besides the radius ratios of the cation and polarization of the halide anion as mentioned in the case of Ag-halides. Similarly, TiX_6^{-2} ions have different colours as in K_2TiX_6 :

K_2TiF_6	Colourless
K_2TiCl_6	Yellow
K_2TiBr_6	Red
K_2TiI_6	Deep red

These colours (spectra) are due to the excitation of electrons in the large halide ion to the metal orbitals. The energy of excitation in iodides is the least and hence the longest wavelengths of absorption for which these are deeply coloured.

Summary of the comparison of properties of the halogens

(1) The valence levels of halogens contains s^2p^5 electrons.

(2) Many of the physical and chemical properties of the halogens can be explained on the basis of their relative sizes.

(3) The colours of the halogens are due to the absorption of visible light leading to the excitation of outer electrons. This trend is indicated by their ionization potential.

(4) The melting and boiling points of halogens can be explained on the basis of intermolecular van der Waals' forces between the halogen molecules.

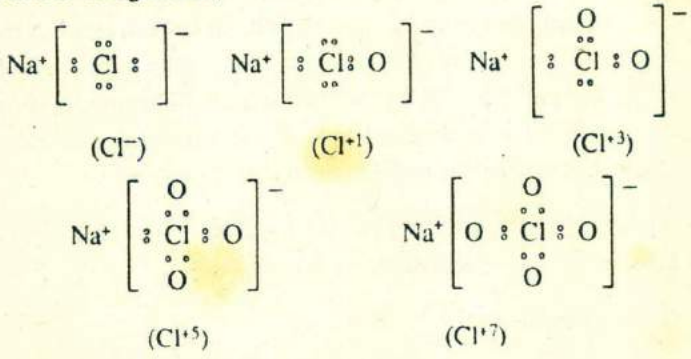
(5) The stability of the halogen molecules is dependent upon the dissociation energy. F_2 has the lowest heat of dissociation and Cl_2 has the highest value which decreases in the case of Br_2 and I_2.

(6) Halogens with high atomic numbers have greater tendency to use outer d-orbitals to form multiple bonds.

(7) Halides of the same metals exhibit different bonding character. Fluorides are more ionic whereas iodides are more covalent.

(8) The halides of large ionic radii are deeply coloured whereas the lower halides are colourless.

Oxidation states : The range of the oxidation states of halogens varies from −1 to +7, although −1 state is predominant. But compounds having +1, +5 and +7 states are also formed. Other oxidation states are known in some cases but +2 state is non-existent. F does not show positive oxidation states and Br is never +7. In water solutions the valence states are −1, +1, +3, +5 and +7 (i. e., difference in 2 units). This is mainly due to (i) covalent halogen-to-oxygen bonds and (ii) coordination of an additional oxygen atom to a lone pair of electrons of halogen thus,



Not many compounds are known which have even oxidation states of halogen. ClO_2 has +4 state of Cl. F_2O_2 is ill-defined as +2 for F and Cl_2O_6 has +6 oxidation state for Cl. These may be regarded as peroxides.

The odd oxidation states arise due to the stability of electronic structures involving pairs of electrons either shared or unshared. The odd oxidation states are generally exhibited by odd groups. ClO_2, BrO_2 and IO_2 having oxidation number +4 for the halogens have odd number of electrons in their molecules. Table 22.3 shows the various oxidation states of halogens in well-known compounds.

Table 22.3. Oxidation states of halogens.

Oxidation states	*F*	*Cl*	*Br*	*I*
−1	NaF	NaCl	NaBr	NaI
0	F_2	Cl_2	Br_2	I_2
+1	—	HClO	HBrO	HIO
		Cl_2O	Br_2O	—
+2	—	—	—	—
+3	—	$HClO_2$	—	
+4	—	ClO_2	BrO_2	IO_2
+5	—	$HClO_3$	$HBrO_3$	HIO_3
				I_2O_5
+7	—	$HClO_4$	—	H_5IO_6
		Cl_2O_7		

Anomalies of fluorine : Fluorine differs in many ways from other halogens. For instance, F does not form oxyacids and oxysalts. It can not be prepared by the general method of formation of other halogens. There are numerous insoluble fluorides, such as those of Ca, Mg, Ba, Sr, lanthanides and actinides. F is the only halogen which exhibits hydrogen bonding and forms only one covalent bond. These anomalies may be attributed to the following reasons :—

(1) The highest electronegativity of F (4.0) is greater than that of oxygen (3.5). Other halogens are less electronegative than oxygen.

(2) Small size of the F atom.

(3) F_2 molecule has low bond energy.

(4) F has no **d** orbitals available.

(5) The reaction of F with other element is highly exothermic (high bond energy).

(6) Insolubility of most fluorides is due to high lattice energies of their three-dimensional network structures. The higher halides have either chain or layer structures.

Chemical properties of the halogens : The chemical properties of the halogens may be summarized in some of the important reactions which take place with other substances. All the reactions of halogens are normally oxidizing actions.

(a) Reaction with hydrogen : All halogens react with hydrogen, although under different conditions giving hydrogen halides :

$$X_2 + H_2 = 2HX \qquad (X = \text{halogens})$$

The reaction of F_2 is very vigorous ; Cl_2 reacts in presence of light. Br_2 reacts readily but I_2 is not very reactive because HI formed is unstable.

(b) Reaction with oxygen : Halogens form a number of oxides by indirect reactions and are discussed under the oxides of halogens.

(c) Reaction with water : All the halogens give HX and HOX with water except F_2:

$$Cl_2 + H_2O = HCl + HOCl$$

But F_2 reacts violently with water to give oxygen flouride, OF_2 :

$$F_2 + H_2O = OF_2 + H_2$$

(d) Reactions with acids : No significant reaction.

(e) Reactions with alkalies : Different salts of oxyacids of halogens are formed under different conditions.

(f) Reactions with metals : Almost all metals react with halogens at various conditions and with different rates. Some react very vigorously and others

slowly under heated conditions. They normally form halides of the metals with high oxidations state :

$$2Fe + 3Cl_2 = 2FeCl_3$$

or generally, $2M + nX_2 = 2MX_n$ (M = metal)

(g) Reactions with non-metals : S is converted to S_2Cl_2 and P is changed to PCl_3 or PCl_5 by the reaction with Cl_2. All halogens show this behaviour.

(h) Reactions with organic compounds : Hydrocarbons burn in Cl_2 gas to form HX and free carbon. Unsaturated organic compounds give important reactions with halogens.

(i) Reactions between halogens : The halogens react among themselves giving a large number of compounds. These are known as interhalogen compounds.

(j) Solubility in organic solvents : Cl_2, Br_2, and I_2 dissolve in many organic solvents. I_2 gives different colour in different solvents. Thus in alcohol it is brown but in CCl_4 or CS_2 it is violet due to molecular I_2. The colour is due to excitation of electrons and breaking of I—I bonds. In aqueous alkali, complete breaking of I—I bonds leads to a colourless solution.

The oxidation reactions of halogens : As pointed out before, oxidations by the halogens are the important and familiar reactions. These may be termed as *fluorination, chlorination, bromination and iodination* for the reactions with F_2, Cl_2, Br_2, and I_2 respectively. Fluorination is the most vigorous and iodination is the least vigorous, but this depends on the materials with which the halogen reacts. Generally the reactions are termed as *halogination.*

When halogens react with covalent compounds giving products which are only halides, the reactions are known as *halogenolysis.* Thus F_2 oxidizes organic compounds, such as C_2H_6, to produce HF and CF_4 by *fluorinolysis* and Cl_2 oxidizes CS_2 to CCl_4 and S_2Cl_2 :

$$H_3C—CH_3 + 7F_2 = 6HF + 2CF_4$$

$$CS_2 + 3Cl_2 = S_2Cl_2 + CCl_4$$

Iodine oxidizes many reducing agents in aqueous solutions, such as the active metals and metal ions of lower valence states, e. g, Cr^{+2}, Sn^{+2} and also negative ions, like SO_3^{-2}, $S_2O_3^{-2}$ etc., e. g.,

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

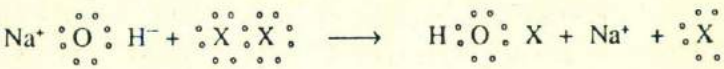
Br_2 being more powerful oxidizing agent oxidizes many reducing agents and also oxidizes an iodide to free I_2. Chlorine oxidizes bromides to free Br_2. Fluorine in aqueous solution, not only oxidizes the reducing substances but also H_2O to produce free oxygen gas.

Hydrolysis of the halogens : Halogens react with water in two ways :

$$X_2 + H_2O = HX + HOX$$

$$X_2 + H_2O = 2HX + \tfrac{1}{2}O_2$$

In dilute aqueous alkali solutions, halogens undergo auto-oxidation or, more precisely, a disproportionation reactions in which the halogens are converted to −1 and +1 oxidation states. F_2 does not show this behaviour. The colours of Cl_2, Br_2 and I_2 disappear by hydrolysis in aqueous alkaline solutions :



The elementary halogens again reappear on acidification of the alkali solution indicating reversible process. In hot solutions HOX (hypohalites) are further oxidised (auto-oxidation) to XO_2^- and XO_3^- together with X^- ions. Thus Br_2 in hot alkali solutions gives :

$$3Br_2 + 6NaOH = NaBrO_3 + 5NaBr + 3H_2O$$

With F_2 the hydrolysis results in the formation of oxygen gas.

Sources of Halogens and their Preparations

Occurrence : The occurrence of the elements in nature gives an idea about the chemical properties and reactivities. Halogens do not occur in nature in the free state but always in the most stable ionic state of −1. Halogens are, therefore, the most electronegative elements and do not occur free in nature.

Fluorine, the most reactive of all elements, is found as fluorspar, CaF_2, fluorapatite, $CaF_2.3Ca_3(PO_4)_2$, and cryolite, Na_3AlF_6. Chlorine is always found as chloride in various compounds, such as NaCl, $MgCl_2$, AgCl etc. Bromine is far less abundant and is found as NaBr, KBr and MgBr in sea water and salt deposits. Iodine in sea water is selectively absorbed by sea-weed (Kelp) but the most important source is Chile saltpeter, $NaNO_3$, in which it is found as sodium iodate, $NaIO_3$, and sodium periodate, $NaIO_4$, and it also occurs in brine wells.

Preparation of halogens : All halogens are obtained from their compounds containing negative halides, X^- ions, by oxidation to free halogen, X_2. The oxidation can be carried out by (i) chemical and (ii) electrolytic methods.

Fluorine

Sources : Fluorspar—CaF_2

Cryolite—Na_3AlF_6

Fluorine is prepared both commercially and in the laboratory by the electrolytic method. Since it is highly reactive, it caused the death of several scientists who attempted to prepare fluorine in the early stages.

Commercially F_2 is obtained by the electrolysis of fused KHF_2 or by the electrolysis of anhydrous liquid HF to which KHF_2 is added to conduct electricity through liquid HF which is a nonconductor. HF is obtained from CaF_2 by the reaction of conc H_2SO_4 and KHF_2 is made from HF and KF. A sketch of an electrolytic cell for the production of F_2 is given in Fig. 22—1.

The highly reactive nature of fluorine and the explosive situation created when H_2 and F_2 become mixed during electrolysis are the main drawbacks. The electrodes are separated by means of copper gauze which surrounds the cathode.

All traces of moisture must be excluded because of the vigorous reaction of F_2 with H_2O. The electrolytes, KHF_2 or HF + KHF_2 are electrolysed in the liquid condition (100-200°C). The cell material, such as copper, becomes coated with a layer of CuF_2 and protects the vessel from the reaction of F_2.

Fluorine is produced at the anode and hydrogen is liberated at the cathode :

$$2KHF_2 \xrightarrow{\text{electrolysed}} \underset{\text{at the anode}}{F_2} + \underset{\text{at the cathode}}{H_2} + 2KF$$

(fused)

$$2HF \xrightarrow[+KHF_2]{\text{electrolysed}} \underset{\text{at the anode}}{F_2} + \underset{\text{at the cathode}}{H_2}$$

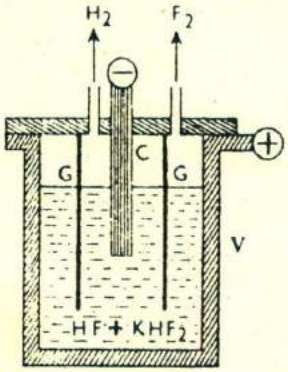


Fig. 22—1. A sketch of the electrolytic cell for the production of fluorine.

V—Electrolytic vessel made of copper which is the anode.

C—Carbon cathode.

G—Copper gauze.

It is to be noted that the electrolysis of an aqueous solution of KHF_2 or NaF does not produce H_2 and F_2 but H_2 and O_2 gas. This is because H_2O is oxidized to O_2, at a much lower voltage (−1.23 volts) than F^- ion which requires a higher voltage to be oxidized to F_2 (− 2.85) volts).

Chlorine

Sources : Rock-salt and common salt in sea water.

Chlorine can be prepared by the chemical and electrolytic methods of oxidation of Cl^- ions from NaCl, other metal chlorides or HCl in aqueous solutions. Cl_2 also be made by the electrolysis of fused NaCl or other chlorides. The electrolysis of brine may be represented by the equation :

$$Na^+ + Cl^- + H_2O \xrightarrow{\text{electrolysis}} Na^+ + OH^- + Cl_2 + H_2$$

Cl_2 is liberated at the anode, usually a carbon rod, and H_2 is evolved at the cathode which is the iron cell itself or mercury. Various designs of cells, such as Nelson, Hooker and Vorce cells are used. Br_2 and I_2 can be prepared by similar electrolytic method as in the case of Cl_2, but these are generally made by chemi-

cal methods. The preparation of chlorine or other halogens (except F_2) by the chemical oxidation depends upon the oxidation potentials of the halogen halide ion couples :

$$2X \longrightarrow X_2 + e^-$$

The standard oxidation potential of the various oxidation-reduction reactions are given in Table 7.2 (page ....). But the oxidation potentials of some oxidation-reduction reactions of ionic systems are given in Table 22.4 in order to understand which oxidizing agent will be more suitable to bring about the oxidation of halide ions into halogens.

The oxidized form of the above reaction systems can oxidize the reduced form of any other system provided the potential is lower or more positive. F_2 is the strongest oxidizing agent with highly negative value of oxidation potential. Cl^- can be oxidized to Cl_2 by $KMnO_4$ and PbO_2 but not by $K_2Cr_2O_7$. The

Table 22.4 Oxidation potentials of some oxidizing systems compared for the preparation of halogens.

Electrode reaction			*Standard oxidation potential* $E°$ *(Volts)*
$2I$	=	$I_2 + 2e$	− 0.53
Fe^{+2}	=	$Fe^{+3} + e$	− 0.77
$2Br^-$	=	$Br_2 + 2e$	− 1.06
$Mn^{+2} + 2H_2O$	+	$MnO_2 + 4H^- + 2e$	− 1.23
$2Cl^-$	=	$Cl_2 + 2e$	− 1.36
$2Cr^{+3} + 7H_2O$	=	$Cr_2O_7^{-2} + 14H + 6e$	− 1.36
$Pb^{+2} + 2H_2O$	=	$PbO_2 + 4H^+ + 2e$	− 1.46
$Mn^{+2} + 4H_2O$	=	$MnO_4^- + 8H^+ + 5e$	− 1.51
$2F^-$	=	$F_2 + 2e$	− 2.80

oxidation potential of MnO_2 is lower than Cl^-/Cl_2 system but the increase of H^+ in the form of HCl and reducing the pressure of Cl_2 gas by heating the reaction mixture, the oxidation of Cl^- to Cl_2 by MnO_2 is brought to completion. This is an example of concentration effect on electrode potential. The oxidation potentials also indicate that F_2 will oxidize Cl^- to Cl_2 which, in turn will oxidize Br^- to Br_2 which will oxidize I^- to I_2. Thus the oxidation potentials

of halide/halogen systems give informations regarding the gradation in the chemical properties of halogens also.

The oxidation of HCl for the preparation of chlorine may be carried out by the following reactions :

1. $4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2$
2. $16HCl + 2KMnO_4 = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$
3. $4HCl + PbO_2 = PbCl_2 + 2H_2O + Cl_2$
4. $2HCl + NaOCl = NaCl + H_2O + Cl_2$

The starting material may be chloride, such as NaCl, which on oxidation with an oxidizing agent in presence of H_2SO_4 gives the reactions represented by the general equations :

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

$$4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2$$

The industrial production of Cl_2 by the *Deacon's Process* involving oxidation of HCl by the atmospheric oxygen in presence of $CuCl_2$ as a catalyst has been replaced by the electrolytic methods. The overall reaction in Deacon's Process in said to involve the equilibrium :

$$4HCl + O_2 \overset{CuCl_2}{\rightleftharpoons} 2H_2O + Cl_2$$

The catalyst, $CuCl_2$, functions as shown by the equations :

$$2CuCl_2 = Cu_2Cl_2 + Cl_2$$

$$Cu_2Cl_2 + O = CuO.CuCl_2$$

$$CuO.CuCl_2 + 2HCl = 2CuCl_2 + H_2O$$

Bromine

Sources : Magnesium bromide, $MgBr_2$ (in sea water).

Brom-carnallite, $MgBr_2.6H_2O$ (in carnallite).

The commercial preparation of bromine form bromides from sea-water or carnallite is done by oxidizing action of chlorine. The pH value is adjusted

between 1—4 with H_2SO_4, and then treated with chlorine. A stream of air is blown to free the liberated bromine which is absorbed in Na_2CO_3 solution. The solution is distilled after acidification :

$$Cl_2 + 2Br^- \rightarrow Br_2 + 2Cl^-$$

$$3Br_2 + 3CO_3^{-2} \rightarrow 5Br^- + 5BrO_3^- + 3CO_2$$

$$5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

Chlorine present is removed from the bromine by reaction with a bromide, such as $FeBr_3$. Further purification from chlorine and iodine is carried out by distilling it with KBr and ZnO which removes chlorine and iodine respectively.

Iodine

Sources : Sea-weed (Kelp)

Chile saltpeter ($NaNO_3$ contains $NaIO_3$)

Burnt sea-weed contains alkali iodide, such as NaI, from which iodine is obtained by heating with an excess of H_2SO_4 and MnO_2. The iodine vapours are condensed in receiver known as *eludels*.

Iodine is mostly obtained by the sulphite reduction of iodates in aqueous solution :

$$2NaIO_3 + 5NaHSO_3 \rightarrow 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2$$

Iodine is purified by sublimation over KI.

Astatine

It occurs in very small amount in nature due to the disintegration of ^{215}Po and ^{218}Po. But astatine has not been isolated from natural sources. It has been prepared from bismuth by bombardment with α-particles.

$$Bi^{209} + He^4 = At^{211} + 2n^1$$

Astatine is radioactive with half-life of 8.3 hours. As would be expected, astatine is a solid element more metallic than iodine.

The solid is volatile and is soluble in carbon disulphide and tetrachloride. Elementary astatine is the weakest oxidizing agent of all the halogens.

Uses of Halogens

Fluorine : F_2 is used in—(i) The productions of fluorocarbon compounds used as lubricants, insecticides etc. Thus Freon, CCl_2F_2, is used as a refrigerant, CCl_3F is an insecticide. Teflon is a plastic having C_2F_4 units in the polymer. (ii) The production of UF_6, SF_6 etc. (iii) The production of ClF_3, a liquid incendiary for war purposes.

Chlorine : Cl_2 used for —(i) bleaching wood pulp and cotton cloth; (ii) chlorinating agents for water; (iii) chlorinating agents for producing organic compounds, such as CCl_4, $CHCl_3$ etc.

Bromine : Br_2 is used in —(i) the manufacture of ethylene dibromide, an antiknock gasoline along with lead tetra-ethyl, $Pb(C_2H_5)_4$; (ii) the production of organic dyes; (iii) the production of AgBr for photography.

Iodine : I_2 is used in—(i) the production of iodoform, CHI_3 ; (ii) the preparation of *tincture of iodine* and (iii) a vast number of medicinal compounds.

Some Important Compounds of Halogens

Hydrogen halide, HX : Both HF and HCl are obtained by the action of concentrated H_2SO_4 on their readily available salts, NaCl and CaF_2. But HBr and HI can not be prepared by the analogous methods since HBr and HI are oxidized to Br_2 and I_2 in concentrated H_2SO_4. Although H_2 and F_2 will react vigorously to form HF, the reaction is too violent to be adopted as a method of preparation of HF.

General Methods of Preparation of HX

1. By direct union of the the elements : The general equation for the reaction of hydrogen and halogen is :

$$H_2 + X_2 = 2HX$$

The heat of formation of HX rapidly decreases with increasing atomic number of halogens. As mentioned above, HF is not prepared by this method. But HCl is commercially produced by combustion of hydrogen, H_2, with chlor-

ine in burners specially designed for this purpose. Both H_2 and Cl_2 are obtained by the electrolysis of brine.

The reaction $H_2 + Br_2 \rightleftharpoons 2HBr$ is much less vigorous and the production of HBr involves heating the mixture of H_2 and Br_2 to 200°C is contact with catalyst, such as Pt or C, and using excess of H_2 to force the equilibrium reaction towards HBr.

HI is not prepared by this method because of the slow reaction and decomposition at equilibrium :

$$H_2 + I_2 \rightleftharpoons 2HI$$

2. By the action of conc H_2SO_4 or conc H_3PO_4 on metallic halide : This is the most convenient method of preparation of HF and HCl.

HF is prepared by heating a mixture of the mineral fluorite, CaF_2, and conc H_2SO_4 in a lead or platinum retort :

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

HF evolved is absorbed in water forming hydrofluoric acid. This is stored in bottle made of lead, wax, plastic or polythene, because HF acts upon glass and other metals. Pure anhydrous HF can be obtained by heating KHF_2 :

$$KHF_2 = KF + HF$$

HCl is also made in the laboratory and commercially by the reaction of NaCl with conc H_2SO_4 :

$$NaCl + H_2SO_4 = HCl + NaHSO_4$$
$$NaCl + NaHSO_4 = HCl + Na_2SO_4$$

HCl is distilled off because it is more volatile than H_2SO_4 .

HBr and HI cannot be prepared by the action of conc H_2SO_4 on a bromide or iodide because HBr and HI are reducing agents. Some HBr and HI produced react with hot H_2SO_4 as follows :

$$NaBr + H_2SO_4 = NaHSO_4 + HBr$$
$$2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2$$
$$NaI + H_2SO_4 = NaHSO_4 + HI$$
$$8HI + H_2SO_4 = H_2S + 4I_2 + 4H_2O$$

HI is a stronger reducing agent than HBr. Hence the reduction of H_2SO_4 to H_2S in the case of HI and to SO_2 by HBr. But HI also produces some SO_2 and elementary S.

HBr and HI are commonly prepared by the action of a soluble metal bromide or iodide with H_3PO_4 which is non-volatile and non-oxidizing acid :

$$NaBr + H_3PO_4 = HBr + NaH_2PO_4$$

$$NaI + H_3PO_4 = HI + NaH_2PO_4$$

3. By the hydrolysis of non-metallic halides : Some covalent halides of non-metals are hydrolysed to give HX. Thus hydrolysis of PCl_3, PBr_3, PI_3, SCl_4 etc. gives the respective HX. This method is particularly useful for the preparation of HBr and HI :

$$PBr_3 + 3H_2O = H_3PO_3 + 3HBr$$

$$PI_3 + 3H_2O = H_3PO_3 + 3HI$$

4. By the halogenation of hydrocarbons : Except HI, other hydrogen halides are obtained as by-products when F_2, Cl_2 and Br_2 react with saturated hydrocarbons in presence of a catalyst for the formation of halogenated hydrocarbons. When ethyl chloride is manufactured, HCl is obtained as a by-product in large quantity :

$$C_2H_6 + Cl_2 = C_2H_5Cl + HCl$$

5. By reduction with H_2S or H_2SO_3 : This method is suitable for producing HBr and HI in aqueous solution. The reactions involved are :

$$Br_2 + H_2S = 2\,HBr + S$$

$$Br_2 + H_2SO_3 + H_2O = 2\,HBr + H_2SO_4$$

$$I_2 + H_2S = 2\,HI + S$$

$$I_2 + H_2SO_3 + H_2O = 2\,HI + H_2SO_4$$

The elementary S produced is filtered off and the solution is concentrated or distilled.

General Properties of Hydrogen Halides

Anhydrous HF, HCl, HBr, HI are colourless gases, having penetrating odour and fume in moist air. Pure HX are non-conductors of electricity and extremely soluble in water. The solubility in H_2O is due to the reaction :

$$HX + H_2O = H_3O^+ + X^-$$

because H_2O is more basic and O is more electronegative than Cl, Br. and I. Hydrofluoric acid, HF, behaves differently and H—F bond has some unique properties. Hydrogen halides in aqueous solutions are generally known as *hydrohalic acids.*

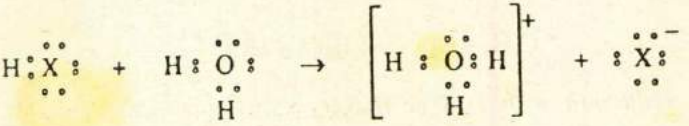
HX in aqueous solutions reacts with metals above H in the E. M. F. series giving oxidation-reduction reaction of the type :

$$\overset{+1}{2HX} + \overset{0}{Zn} = \overset{+2}{ZnX_2} + \overset{0}{H_2}$$

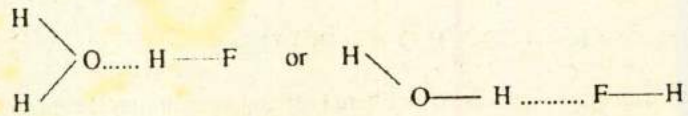
They react with bases to form salt and water. HF in aqueous solution reacts with SiO_2 and also with constituent of glass, $CaSiO_3$, evolving SiF_4 (a volatile gas) :

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

The ionization of HX in water as shown by the equation :

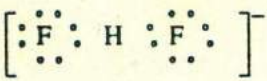


depends upon H—X bond strengths as compared to H—O bond strength in H_3O^+ ion. HF bond is as strong as H—O and HF is not completely ionized. This is due to greater electronegativity of F than that of O. HF molecule is strongly bonded to H_2O by hydrogen bonding :



The bond strength in HCl, HBr and HI are gradually much weaker as compared to H—O. The interatomic distance in HF is also much smaller than that of HI.

Apart form the above considerations the high electronegativity of F is responsible for the association in liquid HF discussed earlier. Therefore, it is liquid at ordinary temperature with higher boiling point than any other HX. The hydrogen bonding in HF is responsible for the formation of many metal fluorides to form hydrogen difluorides, such as $NaHF_2$, KHF_2 etc. HF_2^- ion is represented as :

 or $[F^- H^+ F^-]^-$

The Cl, Br and I atoms in HCl, HBr and HI are much less electronegative and their sizes increase to a great extent as compared to that of F. Hydrogen bonding, therefore, is not significant in these cases.

Some of the properties of hydrogen halides are given in Table 22.5 for the sake of comparison.

Table 22.5 Some properties of hydrogen halides.

Properties	*HF*	*HCl*	*HBr*	*HI*
Molecular weights	20.008	36.465	80.924	127.92
Boiling point (°C)	20	− 85	− 67	− 35
Melting point (°C)	− 83	−114	− 87	− 51
Solubility in H_2O (g/100g. of H_2O)	98(−10°)	93(−15°)	221(0°)	425(10°)
Heat of formation Kcal/mole	64.00	22.00	8.70	− 5.90
Dielectric constant of liquid	66	9	6	3
% dissociation at 1000°C	—	3×10^{-7}	0.003	19

Metal halides : All metals form halides and there are great variations in their properties. For instance, alkali metals, alkaline earth metals of higher

atomic weights, all metal fluorides and some of the transition metal halides are ionic compounds.

These halides have electrical conductivities in the fused state and have high melting and boiling points and those soluble in water are not hydrolysed. Thus Na-halides are good examples of Fajan's rule as given by the melting points : NaF—993°C, NaCl—801°C, NaBr—775°C, NaI—651°C. But halides of metals with high charge-to-size ratios are covalent in character. These are $AlCl_3$, $SnCl_4$, $TiCl_4$ etc. and are volatile, soluble in organic solvents, have no electrical conductivity and are extensively hydrolysed in water. Some halides are in-between the above two types. Thus $FeCl_3$ is volatile, hydrolysed in water, soluble in organic solvents, but conduct electricity in the fused state. Solubility of halides in water differs to a great extent and even halides of the same metal have different solubility. Thus AgF is soluble in water but AgCl, AgBr and AgI are insoluble. CaF_2 is insoluble but $CaCl_2$, $CaBr_2$ and CaI_2 are soluble. Similarly, Hg_2Cl_2 and $PbCl_2$ are insoluble.

The properties of metal halides are convincing examples of the application of Fajan's rules.

Uses of hydrohalic acids and halides

Hydrofluoric acid : HF is used—(i) in etching and writing on glass; (ii) in analysis of rocks and minerals ; (iii) in the production of fluorides, such as BF_3, UF_6 etc. (iv) CaF_2, NaF etc. are used as fluxes. (iv) consumption of blast furnace slag $CaSiO_3$ to SiF_4 (v) Producing freons such as CF_2Cl_2.

Hydrochloric acid : HCl is the most important acid in industry. It is used—(i) in the formation of metal chlorides ; (ii) in the manufacture of dyes, glucose etc.

Hydrobromic acid : HBr is used—(i) in analytical chemistry and (ii) in the synthesis of organic compounds.

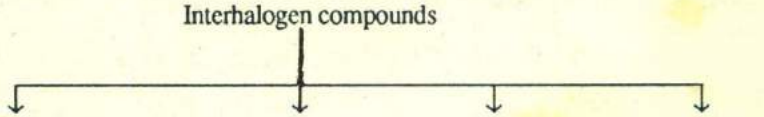
Hydroiodide acid : HI is also used for the same purpose as HBr.

Interhalogen compounds :

The compounds formed by the combination of different halogens are called *Interhalogen Compounds*. Examples of interhalogen compounds are given below :

ICl	BrCl	ClF
IBr	BrF	ClF_3
ICl_3	BrF_3	
IF_5	BrF_5	
IF_7		

Interhalogen compounds are classified as follows :



AB type	**AB_3 type**	**AB_5 type**	**AB_7 type**
ClF	ClF_3		IF_7
BrF	BrF_3	BrF_5	
BrCl		IF_5	
ICl	ICl_3		

It is interesting to note that interhalogen compounds consist of one atom of heavier halogen bonded to a number of the lighter halogen. The larger-sized I atom has greater number of interhalogen compounds and also greater number of halogen atoms around it. The great difference in electronegativity between halogens gives rise to these compounds. The larger-sized halogens are positive and form compounds with more negative ones. Thus we have IF_7, BrF_5 and ClF_3. Most of these compounds are unstable and extremely reactive like halogens. Hydrolysis in basic reactions give halide of the smaller halogen and oxy-halide from the larger halogens :

$$ICl + NaOH = NaCl + HOI$$

ICl, ICl_3 are formed by the oxidation of I_2 or I^- ion in conc HCl. This may be made by the reaction, $I_2 + Cl_2 = 2ICl$. Iodine chloride, ICl, is a liquid at room temperature. Iodine trichloride is obtained by the reaction $I_2 + 3Cl_2$ (excess) = $2ICl_3$. Iodine trichloride, ICl_3 is a yellow solid and can also be obtained by the reaction :

$$I_2O_5 + 10HCl = 2ICl_3 + 5H_2O + 2Cl_2$$

IBr is obtained by the direct reaction of $I^- + Br_2 = 2IBr$. Chlorine fluoride, ClF, is obtained by reaction of HF and Cl_2 at the temperature of liquid air. Similarly, Br or HBr on reaction with F_2 gives BrF_3 as a colourless liquid. BrF_5 is made from BrF_3 and fluorine. IF_5 and IF_7 are obtained from I_2O_5 and F_2.

The bonding in the interhalogen compounds do not follow normal valence or bonding rules. ClF_3 is supposed to use sp^3d orbitals of Cl.

Similarly, BrF_5 uses sp^3d^2 octahedral bonding of Br and IF_7 has sp^3d^3 hybrid orbitals of I.

Polyhalides :

Compounds in which halogens or interhalogens become associated together are called *Polyhalides*. Thus KI_3 is a K-polyiodide (tri-iodide). Compounds containing I_5^-, I_7^- and I_9^-, Br_3^-, Cl_3^- etc. have also been prepared. The larger polyhalides are generally found in compounds having large cations, such as Cs^+I_7, Rb^+I_9, $(C_2H_5)_4N^+I_7^-$ etc. Br_3^- and Cl_3^- are unstable ions ; F_3^- does not exist. The well-known examples of polyhalides of two different halogens are $KICl_2$, $CsIBr_2$, $CsClBr_2$, CsIBrCl, $KICl_4$ etc. These are known as mixed polyhalides.

It is well-known that the solubility of iodine in water is greatly increased by adding KI. It has been shown that the deep-brown solution contains I_3^- anion (tri-iodide ion). Here iodine and iodide ion combine giving the reversible reaction :

$$I^- + I_2 \rightleftharpoons I_3^-$$

The combination is due to induced dipole action of I^- ion on I_2. The negative I^- ion when close to a large I_2 molecule, disturbs the electronic arrange-

ments forming the induced dipole leading to the attraction between the negative end of the iodide ion and the positive end of the polar iodine molecule.

The Oxides and Oxyacids of Halogens

The oxides and oxyacids of halogens and their salts are formed by sharing of electrons with oxygen. These compound are important oxidizing agents.

Oxides of Halogens : A number of binary compounds of halogens and oxygen have been made by indirect methods since the two elements do not combine directly. These are :

OF_2	Cl_2O	Br_2O	I_2O_4
O_2F_2	ClO_2	Br_3O_8	I_4O_9
	Cl_2O_6	BrO_2	I_2O_5
	Cl_2O_7		

Because oxygen is more electronegative than Cl, Br and I, their oxygen compounds are halogen oxides. But F compounds are oxygen fluorides because F is more electronegative than oxygen.

Oxygen fluorides : Oxygen difluoride, OF_2, is a colourless gas and oxygen monofluoride, O_2F_2, is a red liquid. OF_2 is a covalent compound having O and F in + 2 and −1 oxidation states respectively. OF_2 is formed when F_2 reacts with NaOH solution :

$$2F_2 + 2NaOH = 2NaF + OF_2 + H_2O$$

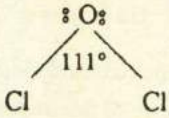
OF_2 is immediately separated. It is a powerful oxidizing agent. The aqueous solution of OF_2 is not acidic indicating that it is not the anhydride of an acid.

Oxides of chlorine : *Chlorine monoxide* Cl_2O, is a yellowish red gas which explodes violently on heating. This is prepared by passing Cl_2 gas over HgO (300 — 400°C)

$$2Cl_2 + 2HgO = HgCl_2. + Cl_2O$$

Cl_2O is the anhydride of HClO (Hypochlorous acid) and reacts readily with water to form HOCl. The structure of Cl_2O is based on the use of sp^3 hybrid

bonds of O. The angle ClOCl is 111° greater than tetrahedral angle due to electronegativity difference in O and Cl atoms.



Chlorine dioxide : ClO_2, is a reddish-yellow gas and explodes violently when pure. It is handled in diluted form with air or CO_2. It is formed along with $HClO_4$, when $KClO_3$ is treated with conc H_2SO_4. This method is dangerous and oxalic acid is conveniently used in the reactions :

$$4KClO_3 + 4H_2SO_4 = 4KHSO_4 + 4ClO_2 + O_2 + 2H_2O$$

$$2KClO_3 + 3H_2C_2O_4 = 2ClO_2 + 2CO_2 + 2H_2O + 2KHC_2O_4$$

A convenient commercial method involves the reaction of sodium chlorite with Cl_2 diluted with air :

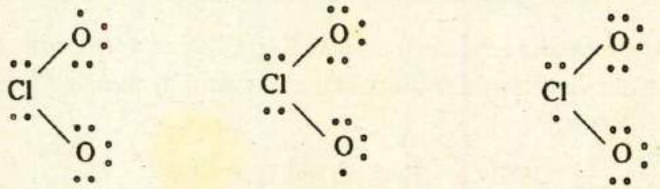
$$2NaClO_2 + Cl_2 = 2NaCl + 2ClO_2$$

Pure ClO_2 is obtained by the reaction :

$$Cl_2\,(dry) + 2AgClO_3 \longrightarrow 2AgCl + 2ClO_2 + O_2$$

ClO_2 is now an important commercial product and is used as an antiseptic, in water purification and bleaching of cellulose materials and high grade paper pulp. Also in making unshrinkable woolen fabrics.

ClO_2 is an odd molecule, but it is not dimerized. It contains a three-electron bond and has one unpaired electron. The formula can be written in several forms. It is the only compound in which Cl has +4 oxidation state :



The single electron floats between the two O atoms and the Cl atom. Cl atom in ClO_2 uses possible sp^3d hybrid bonds.

When ClO_2 is dissolved in alkaline solution, alkali chlorate and chlorites are formed.

Chlorine heptoxidi Cl_2O_7 : This is obtained as an oily liquid by dehydrating $HClO_4$ over P_2O_5 at $-10°C$ and distilling :

$$4HClO_4 + P_4O_{10} = 2Cl_2O_7 + 4HPO_3$$

Cl_2O_7 slowly reacts with water giving $HClO_4$. Cl_2O_7 is composed of two ClO_4 tetrahedra joined by an O atom. $O_3Cl—O—ClO_3$

The oxides of bromine are not well established.

Iodine Pentoxide : I_2O_5 is the most stable of all the halogen oxides. It is made by evaporating HIO_3 (dehydrating) :

$$2HIO_3 = I_2O_5 + H_2O$$

I_2O_4, I_2O_5 and I_4O_9 are stable solids.

Basic Iodine : Oxides of iodine are unreactive and it has been suggested that these are ionic compounds. Thus I_4O_9 has been formulated as $I(IO_3)_3$. Iodine is the most metallic of the halogens (except At). Since the oxides of iodine are ionic compounds these are most stable. There are other compounds in which iodine behaves as cation. Both +1 and +3 oxidation states are found but +3 oxidation state is the most stable. Thus the acetate, phosphate, nitrate and perchlorate etc. of I^{+3} have been isolated :

$$I(CH_3COO)_3,\ IPO_4,\ I(NO_3)_3,\ I(ClO_4)_3.2H_2O$$

These are analogous to trivalent Al^{+3} and are hydrolysed easily disproportionating into iodate and I_2. Chloride, pyridine and olefine compounds of I^{+1} are formed and resemble those of Ag^{+1} compounds :

$$[I(Py)]^+ Cl^- \qquad\qquad I(C_2H_4)Cl$$

Oxyacids of the Halogens and their Salts

Oxyacids of fluorine or their salts are unknown. Chlorine has greater tendency to form oxyacids than Br_2 and I_2. The series of oxyacids formed by Cl_2 Br_2 and I_2 are given in Table 22.6

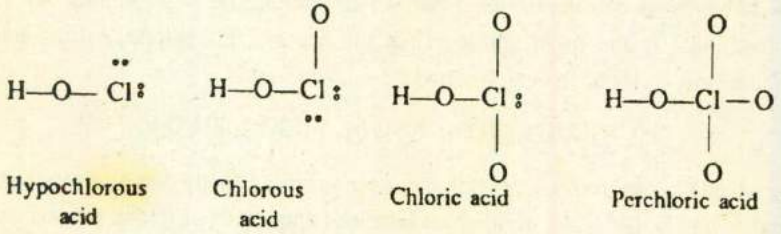
Table 22.6. Oxyacids of halogens.

Oxidation states	Cl_2	Br_2	I_2
+1	HClO	HBrO	HIO
+3	$HClO_2$	$HBrO_2$	—
+5	$HClO_3$	$HBrO_3$	HIO_3
+7	$HClO_4$	—	HIO_4, H_5IO_6

The greater the number of oxygen in the oxyacid of halogens or their salts, the greater is their stability towards heat. But the acids are more unstable than their corresponding salts. The reactivity also is dependent on the number of oxygen atoms and decreases with increasing number of oxygen atoms. Thus HXO is more reactive than HXO_4. But the strength of acids in terms of ionization is greater, the larger the number of oxygen atoms in the molecule. Thus HXO_4 is a stronger acid than HXO_3 which is a stronger acid than HXO_2 or HXO. The sequence of strength of acid is as follows :

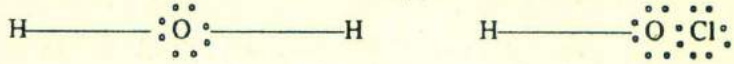
$$HXO_4 > HXO_3 > HXO_2 > HXO$$

The acid molecules contain H linked to the halogen through an oxygen atom. Thus in the case of chlorine, we have,



The bonds between H and O are polar in nature and all the oxygen atoms are linked to the halogen by covalent bonding. The oxidation states of the halogen are dependent on the number of electrons shared with oxygen. Thus in HClO, $HClO_2$, $HClO_3$ and $HClO_4$, chlorine shares 1, 3, 5 and 7 electrons respectively with oxygen atoms. Hence the corresponding oxidation states of Cl are +1, +3, +5 and +7 in these acids or their salts. The positive oxidation state of halogen lead to the shifting of the bonding electrons from hydrogen and the tendency to

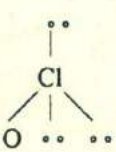
lose a proton to water in aqueous solution is greatly increased. The electron density is shifted away from H and becomes concentrated around Cl and O:



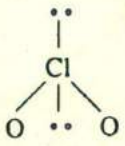
The greater the number of oxygen atoms around the halogen, the greater is the shift of electron density around it. Hence the acid strength increases in the case of, say, perchloric acid, $HClO_4$ as mentioned above.

It has also been observed that large size of the halogen and small values of electronegativity give rise to weaker acids and lower stability for the corresponding ions. Thus HClO is a stronger acid than HBrO which is stronger than HIO. Similarly, hypoiodite ion is much less stable than hypobromite and hypochlorite ions and are hydrolysed and decomposed readily.

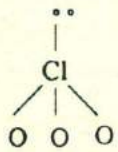
The structure of ClO^-, ClO_2^-, ClO_3^- and ClO_4^- ions are tetrahedral with O atom occupying 1, 2, 3, 4 corners respectively. Thus the configurations may be represented as



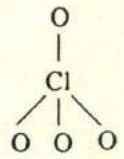
Hypochlorite ion
(ClO^-)



Chlorite ion
(ClO_2^-)



Chlorate ion
(ClO_3^-)



Perchlorate ion
(ClO_4^-)

But with iodine, more than four oxygen atoms can be accommodated. IO_4^- ion is tetrahedral like ClO_4^- ion. But IO_6^- ion is octahedral with the oxygen at the corners of an octahedron.

All the oxyghalogen anions are good oxidizing agents.

Hypohalous Acids and Hypohalites

Hypohalous acid, HXO, has not been obtained in the pure state but can be made in aqueous solutions. The aqueous solutions of HXO are prepared by hydrolysis of the free halogens. Cl_2 has greater tendency to undergo the hydrolysis than other halogens :

$$X_2 + H_2O \rightleftharpoons HX + HXO$$

Addition of cold and dilute alkali shifts the equilibrium towards the right :

$$X_2 + 2NaOH = NaX + NaXO + H_2O$$

At higher temperatures NaXO are unstable and undergo disproportionation :

$$\underset{\text{hypohalite}}{3XO^-} = \underset{\text{halide}}{2X^-} + \underset{\text{halate}}{XO_3^-}$$

Solutions of HClO is prepared by several methods as given by the equation :

$$HgO + 2Cl_2 + H_2O = HgCl_2 + 2HClO$$

This is a general method and all HXO may be prepared by the action of halogens on moist HgO. $CaCO_3$ is also used :

$$CaCO_3 + H_2O + 2Cl_2 = CaCl_2 + 2HClO + CO_2$$

Sodium Hypochlorite, NaClO, is produced on a large-scale by the electrolysis of aqueous NaCl under the condition that NaOH and Cl_2 formed are mixed at low temperature. The solution of sodium hypochlorite contains NaCl and is sold as such for the purpose of bleaching agent and antiseptic.

NaOCl is used as an oxidizing agent for converting Cr^{+3} to chromate, Pb-salts to PbO_2, arsenites to arsenates, bleaching paper pulp and cellulose etc.

Bleaching powder, $CaOCl_2$ or $CaCl(OCl)$: It is a salt which contains both Cl^- and OCl^- ions, It is manufactured by the reaction of Cl_2 with slaked lime. Several designs of the manufacturing plants have been used. The principle of the process is to push slaked lime, $Ca(OH)_2$ from one direction while Cl_2 gas is passed from the other direction based on counter current

principle. Thus in Bachmann plant slaked lime is introduced from the top of a tower containing shelves and rotating blades and Cl_2 with hot air is passed from the bottom of the tower upwards. The intimate mixing of Cl_2 with $Ca(OH)_2$ is thus achieved :

$$Ca(OH)_2 + Cl_2 = CaCl(OCl) + H_2O$$

Bleaching powder is a yellow powder, has the smelling of chlorine and has been used for a long time as a bleaching agent and a source of chlorine and hypochlorous acid. Also used for sterilization of water and for manufacture of chloroform.

The average percentage of *available chlorine* in bleaching powder is about 40% (theoretical 49%). The available chlorine is determined by mixing a known volume of bleaching powder suspension with excess of KI and titrating the liberated iodine with $Na_2S_2O_3$ solution.

$$CaOCl_2 + 2KI + CH_3COOH = (CH_3COO)_2Ca + 2KCl + I_2$$

Calcium hypochlorite, $Ca(ClO)_2$: This is also known as high test hypochlorite (H. T. H.). This is obtained from $CaCl_2$ and NaClO.

$$CaCl_2 + 2NaClO = Ca(ClO)_2 + 2NaCl$$

$Ca(ClO)_2$ is more soluble, more stable and more effective as a bleaching agent than bleaching powder.

Halous Acids and Halites

***Halous acids*, HXO_2** : cannot be isolated in the free form. Only the chlorites give well-defined salts. The reaction of ClO_2 on caustic alkalis gives the products chlorite, ClO_2^- ion and chlorate, ClO_3^- ion :

$$2ClO_2 + 2KOH = KClO_3 + H_2O$$

Thus ClO_2 is not a true anhydride since its Cl atom has an oxidation state different from that exhibited by either chlorite or chlorate ions.

An aqueous solution of $HClO_2$ is obtained by the action of $Ba(ClO_2)_2$ with H_2SO_4 and filtering off $BaSO_4$ precipitate :

$$Ba(ClO_2)_2 + H_2SO_4 = BaSO_4 + 2HClO_2$$

$HClO_2$ is decomposed to HClO and $HClO_3$ at ordinary temperatures indicating disproportionation. The chlorites are prepared by the action of ClO_2 on peroxides:

$$2ClO_2 + Na_2O_2 = 2NaClO_2 + O_2$$

$$2ClO_2 + BaO_2 = Ba(ClO_2)_2 + O_2$$

Bromous acid. $HBrO_2$, is obtained by the action of $AgNO_3$ with excess of Br_2-water :

$$2Br_2 + 2AgNO_3 + 2H_2O = HBrO_2 + 3AgBr + 3HNO_3$$

Halic Acids and Halates

Both *Chloric acid, $HClO_3$, and bromic acid, $HBrO_3$,* are obtained in solution and are decomposed readily. But *iodic acid,* HIO_3, is obtained in the form of colourless crystals soluble in water.

Solutions of $HClO_3$ is readily obtained from barium chlorate by the reaction with H_2SO_4 and filtering. The method is applied to $HBrO_3$ and HIO_3 also :

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3$$

HIO_3 is obtained by oxidizing I_2 with conc HNO_3 :

$$I_2 + 10HNO_3 = 2HIO_3 + 10NO_2 + 4H_2O$$

Chlorine gas oxidizes both Br_2 and I_2 in aqueous solutions to give $HBrO_3$ and HIO_3 solutions :

$$5Cl_2 + Br_2 + 6H_2O = 2HBrO_3 + 10HCl$$

$$5Cl_2 + I_2 + 6H_2O = 2HIO_3 + 10HCl$$

All halic acids are strong acids and active oxidizing agents. $HClO_3$ is decomposed according to the equation :

$$3HClO_3 = HClO_4 + 2ClO_2 + H_2O$$

The halogens react with hot solutions of alkalis producing *halates* and *halides* :

$$2X_2 + 6NaOH = NaXO_3 + 5NaX + 3H_2O$$

$NaXO_3$ may be separated from NaX by fractional crystallisation. Among the alkali halates $KClO_3$ is one of the most important compound.

Potassium chlorate, $KClO_3$: This is obtained when Cl_2 is passed into hot milk of lime and the solution of $Ca(ClO_3)_2$ so formed gives $KClO_3$ on treatment with KCl. $KClO_3$ is less soluble than the Ca-salt :

$$6Ca(OH)_2 + 6Cl_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O$$

$$Ca(CO_3)_2 + 2KCl = 2KClO_3 + CaCl_2$$

The modern method of the production of $KClO_3$ (or other halates as well) is based on the electrolysis of hot halide solutions.

When a solution of KCl is electrolysed at 60—70°C in a cell with a number of electrodes which are close to each other the products of electrolysis, KOH and Cl_2, get mixed with each other giving $MClO_3$. The reaction in the cell is given by the equation :

$KCl + 3H_2O$ + electrical energy = $KClO_3 + 3H_2$ The general equation is, therefore :

$$X^- + 3H_2O \xrightarrow{\text{electrolysis}} XO_3^- + 3H_2$$

Chlorates are normally water soluble, bromates are less soluble and many iodates are insoluble. All halates decompose on heating. $MClO_3$ on strong heating gives O_2 :

$$2KClO_3 = 2KCl + 3O_2$$

On moderate heating $4KClO_3 = 3KClO_4 + KCl$. Bromates and iodates are decomposed in numerous ways. $KClO_3$ is used in the manufacture of matches etc. Bromates and iodates are used as oxidizing agents in analysis.

Perhalic Acids and Perhalates

Perchloric acid, $HClO_4$, and *periodic acid*, HIO_4, are well-defined compounds, but perbromic acid is unknown.

$HClO_4$ and HIO_4 also form well-defined salts which are not formed by bromine.

$HClO_4$ is obtained by adding H_2SO_4 to $KClO_4$:

$$KClO_4 + H_2SO_4 = KHSO_4 + HClO_4$$

$HClO_4$ is distilled under reduced pressure below 92°C. Above 92°C it explodes violently. It is a powerful oxidizing agent in the concentrated and hot condition but the action in dilute and cold solution is slow. $HClO_3$ is turned to $HClO_4$ on slight heating or exposure to light :

$$3HClO_3 = HClO_4 + Cl_2 + 2O_2 + H_2O$$

$KClO_3$ on moderate heating gives $KClO_4$ + KCl from which sparingly soluble $KClO_4$ is separated by leaching out KCl with water.

The perchlorates of Na^+ and K^+ are produced commercially by prolonged electrolysis of hot solutions of NaCl or KCl. The ClO_3^- ion first formed is converted to ClO_4^- ion.

$$ClO_3^- + H_2O \xrightarrow{\text{electrolysis}} ClO_4^- + 2H^+$$

The perchlorates are strong oxidizing agents but less so than the chlorates. $KClO_4$ is used in match industry and explosives. Anhydrous $Mg(ClO_4)_2$ is used as an excellent drying agent.

A number of periodic acids and their salts are known; among these *metaperiodic acids*, HIO_4, and *Paraperiodic acid*, H_5IO_6, are the most important. The larger iodine atom can accommodate more oxygen atoms.

$NaIO_4$ is prepared by oxidation of $NaIO_3$ in hot alkali solutions with Cl_2. Electrolytic method is also used.

It is rather puzzling that so far perbromic acid and perbromates have not been prepared.

MANGANESE

Manganese (Mn), Technetium (Tc) and Rhenium (Re) are the metals of group VIIB. Rhenium has been discovered recently and Technetium is a synthetic

element existing as radioactive isotopes. The electron arrangement in the outer orbitals are the same in the three elements :

Mn (25)—Ar core, ... $3d^5\ 4s^2$

Tc (43)—Kr core, ... $4d^5\ 5s^2$

Re (75)—Xe core, ... $4f^{14}\ 5d^5\ 6s^2$

Comparison of Mn group with halogens

(1) The Mn group elements also have 7 electrons (d^5s^2) in the outermost orbitals as in the case of halogens but the outermost electron groupings in the latter are s^2p^5. (2) The halogens are active non-metals whereas the manganese group are transition metals in which d-levels are being involved. (3) But in the higher oxidation states group VIIA and VIIB have some similarities. Thus Mn_2O_7 and Cl_2O_7 are volatile compounds and explosive. $KClO_4$ and $KMnO_4$ are strong oxidizing agents and form isomorphous crystals.

Extraction of Manganese (Metallurgy)

Sources : (1) Pyrolusite—MnO_2

(2) Braunite—Mn_2O_3

(3) Manganite—MnO(OH) or $Mn_2O_3.H_2O$

(4) Hausmanite—Mn_3O_4

Metallic manganese is obtained by carbon reduction process of MnO_2 which is the chief ore of Mn. Very high temperature is required because MnO first formed is not readily reduced by C :

$$MnO_2 + 2C = Mn + 2CO$$

Nearly pure Mn is obtained by the reduction of MnO_2 by Al (aluminothermic process) :

$$3MnO_2 + 4Al = 3Mn + 2Al_2O_3$$

Pure metal is obtained by the electrolysis of $MnCl_2$ solution with a Hg-cathod. Mn—Hg (amalgam) formed is distilled in vacuum to remove Hg.

Uses of Mn : (1) Production of ferromanganese in steel industry; (2) Production of pure MnO_2 for dry cells.

Alloys of Mn : Since alloys of Mn and Fe are extensively used in the production of steel, such alloys are usually produced instend of the pure metal. These are made by reducing the mixed oxide of MnO_2 and Fe_2O_3 with coke in a blast furnace. The alloy formed is rich in manganese (70—80% Mn) and called *Ferromanganese*. Those products having low percentages of Mn (20—30%) are known as *spiegeleisen* used in steel industry. *Manganin* (Cu—83%, Mn—13%, Ni—4%) is used for making resistance coils. Manganese steel (13% Mn). is very hard and is used for making rails, armour plates etc.

General properties of Mn : It is a grey-white metal and brittle. It is readily oxidized by moist air and decomposes water slowly giving $Mn(OH)_2$ and H_2. It is easily dissolved in dilute acids forming salts of Mn^{+2} ion. Mn forms five oxides and five corresponding series of compounds having oxidation states of +2, +3, +4, +6 and +7. The compounds of Mn, therefore, can be grouped as shown in Table 22.7.

Table 22.7. Different oxides and salts of Mn.

Oxidation states	*Oxides*	*Hydroxide*	*Properties*	*Derivaties*	*Colour*
+2	MnO	$Mn(OH)_2$	Basic	$MnCl_2$ (manganous)	Faint Pink
+3	Mn_2O_3	$Mn(OH)_3$	Weak base	$MnCl_3$ (manganic)	Violet
+4	MnO_2	H_2MnO_3	Weak acid	$CaMnO_3$ (manganite)	Brown
+6	MnO_3	M_2MnO_4	Acidic	K_2MnO_4 (Manganate)	Green
+7	Mn_2O_7	$HMnO_4$	Strong acid	$KMnO_4$ (Permanganate)	Purple

Some Important Compounds of Mn

Manganous Salts : These contain Mn in the +2 state. *Manganous halide*, MnX_2, form beautiful pink crystals. In the anhydrous state these are prepared by the general reactions :

$$Mn + 2HX \xrightarrow{heat} MnX_2 + H_2$$

$$MnO + 2HX \xrightarrow{heat} MnX_2 + H_2O$$

In solution manganous halides are formed by dissolving manganese compounds in halogen acid. These are hydrated compounds :

$$MnO + HCl\,(aq) \rightarrow MnCl_2$$

When an alkali solution is added to Mn^{+2} salts in solution, the pink $Mn(OH)_2$ is precipitated but on exposure to air it is converted to dark brown Mn^{+3} compound of the composition MnO(OH).

Manganous nitrate, $Mn(NO_3)_2$: This is prepared by adding $Ba(NO_3)_2$ to manganous sulphate and filtering off $BaSO_4$:

$$MnSO_4 + Ba(NO_3)_2 \rightarrow Mn(NO_3)_2 + BaSO_4$$

$Mn(NO_3)_2, 6H_2O$ is the common manganous nitrate and is decomposed to MnO_2 when heated.

Manganous sulphate $MnSO_4$: This is prepared by the action of dilute H_2SO_4 on manganese and separated by crystallisation. At room temperature $MnSO_4. 4H_2O$ is obtained. Water is removed easily on heating but $MnSO_4$ decomposes only after heating above 800°C.

Manganese trichloride, $MnCl_3$: Only MnF_3 and $MnCl_3$ are known containing Mn in the +3 state. Bromide and iodide are easily oxidized by Mn^{+3} ion. Even $MnCl_3$ exists as a dark coloured solution which is obtained by the action of HCl on MnO_2 in the cold :

$$MnO_2 + 4HCl \rightarrow MnCl_4 + 2H_2O$$

$$2MnCl_4 \rightarrow 2MnCl_3 + Cl_2$$

$$2MnCl_3 \rightarrow 2MnCl_2 + Cl_2$$

On warming, $MnCl_3$ is decomposed to stable $MnCl_2$ and Cl_2 is evolved. Solutions of complex chlorides are obtained on adding alkali metal chlorides to $MnCl_3$ solutions.

Manganese dioxide (Peroxide), MnO_2 : This occurs naturally as pyrolusite known as *Black oxide*. It is almost pure MnO_2 and the purity of

pyrolusite is determined by the reaction with HCl when Cl_2 is evolved and liberates I_2 from KI to be titrated iodometrically. Alternatively pyrolusite may be reacted with oxalic acid in presence of H_2SO_4 and the excess oxalic is determined by titration with $KMnO_4$ solution.

MnO_2 may be prepared by heating $Mn(NO_2)_2$ to 200°C :

$$Mn(NO_3)_2 \rightarrow MnO_2 + 2NO_2$$

Reduction of $KMnO_4$ in neutral medium also gives MnO_2 :

$$MnO_4^- + SO_3^{-2} \xrightarrow{H_2O} SO_4^{-2} + MnO_2$$

MnO_2 is a black solid which conducts electricity.

It reacts with H_2 or CO to give MnO which is a green solid :

$$MnO_2 + H_2 \xrightarrow{heat} MnO$$

When MnO_2 is heated to 600°C it gives Mn_2O_3 which on further heating to 900°C is converted to Mn_3O_4 with evolution of oxygen :

$$MnO_2 \xrightarrow{600°C} Mn_2O_3 \xrightarrow{900°C} Mn_3O_4$$

Mn_3O_4 behaves as a mixture of MnO and Mn_2O_3. When MnO_2 reacts with alkaline oxide or hydroxide manganites containing MnO_3^{-2} ions are formed :

$$MnO_2 + 2\,OH^- \rightleftharpoons MnO_3^{-2} + H_2O$$

$$MnO_2 + CaO \xrightarrow{heat} CaMnO_3$$

MnO_2 also gives green manganate with alkali when heated in presence of a little oxidizing agent such as KNO_3 :

$$MnO_2 + K_2O + O_2 \xrightarrow{heat} 2K_2MnO_4$$

MnO_2 is converted to permanganate MnO_4^- by oxidizing agents such as Cl_2, PbO_2 etc. :

Uses of MnO_2 : It is used in (1) dry cells, (2) for producing chlorine gas, (3) for producing manganese steel, (4) as a catalyst, (5) in explosives etc.

Potassium manganate, K_2MnO_4 : This is obtained when MnO_2 is fused with alkali hydroxide or carbonate in presence of air or $KClO_3$:

$$2MnO_2 + 4KOH + O_2 = 2K_2MnO_4 + 2H_2O$$

Manganates are green in colour and stable in presence of alkali. $Na_2MnO_4.10H_3O$ is isomorphous with $Na_2SO_4.10H_2O$.

Potassium Permanganate, $KMnO_4$: This is an important compound of Mn. It is prepared from pyrolusite, MnO_2, by first converting it to K_2MnO_4 with K_2CO_3 and air :

$$MnO_2 + K_2CO_3 + O_2 \rightarrow K_2MnO_4 + CO_2$$

When K_2MnO_4 solution is neutralized by adding H_2SO_4 or by passing CO_2 the manganate is converted to permanganate :

$$3\,K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH$$

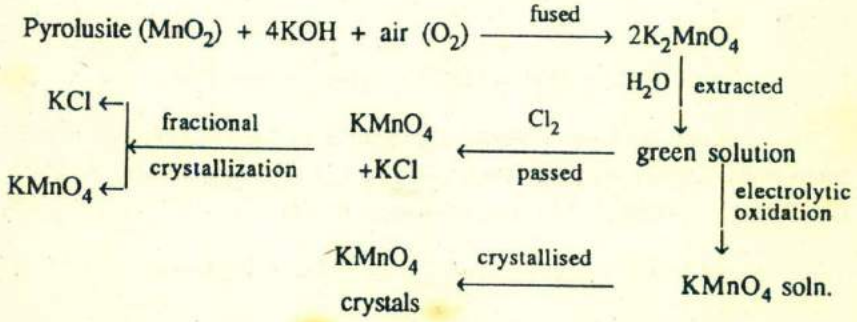
In order to avoid precipitation of MnO_2, permanganate is made by oxidation with Cl_2.

$$2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl$$

K_2MnO_4 is also converted to $KMnO_4$ by electrolytic oxidation between iron electrodes. The oxygen evolved at the anode oxidizes K_2MnO_4 to $KMnO_4$:

$$2K_2MnO_4 + H_2O + O \xrightarrow{\text{electrolysis}} 2KMnO_4 + 2KOH$$

The production of $KMnO_4$ is schematically represented as follows :



Properties of $KMnO_4$: It is a powerful oxidizing agent and is used for oxidation in acidic, neutral or alkaline medium. It is used as a valuable laboratory reagent.

In acid medium, $KMnO_4$ is reduced to Mn^{+2} compounds. The change of oxidation state from Mn^{+7} to Mn^{+2} involves acceptance of 5 electrons by $KMnO_4$. The equivalent weight of $KMnO_4$ in acid medium is $\frac{1}{5}$ of the molecular weight.

In acid medium some of the oxidation reactions are :

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO + 8H_2O$$

$$5Na_2C_2O_4 + 2KMnO_4 + 8H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 8H_2O$$

$$5H_2SO_3 + 2KMnO_4 = 2H_2SO_4 + K_2SO_4 + 2MnSO_4 + 3H_2O$$

It is to be noted that in acid medium HCl and HNO_3 cannot be used since HCl is oxidized to Cl_2 by $KMnO_4$ and HNO_3 itself is an oxidizing agent. Hence H_2SO_4 is generally used for reactions in acid medium.

In neutral medium, $KMnO_4$ changes to MnO_2, i.e., from Mn^{+7} to Mn^{+4} and the solution turns alkaline due to liberation of KOH. The equivalent weight for such reaction is $\frac{1}{3}$ of the molecular weight of $KMnO_4$. The oxidation of NH_3 to N_2 is an example:

$$2KMnO_4 + 2NH_3 = 2KOH + 2MnO_2 + N_2 + 2H_2O$$

In alkaline medium, $KMnO_4$ is mostly used for oxidation of organic compounds. Alkali converts $KMnO_4$ to K_2MnO_4, i. e., change of Mn^{+7} to Mn^{+6}. But K_2MnO_4 is unstable and is further changed to MnO_2 :

$$KMnO_4 + KOH + H_2O_2 = K_2MnO_4 + H_2O + O_2$$

$$6KMnO_4 + KI + 6KOH = 6K_2MnO_4 + 3H_2O + KIO_3$$

$$2K_2MnO_4 + 2H_2O = 2MnO_2 + 4KOH + O_2$$

It is to be noted that the electrode potentials

$$Mn^{+2}/MnO_4^- = 1.52 \text{ Volts}$$

$$MnO_2/MnO_4^- = 1.67 \text{ volts}$$

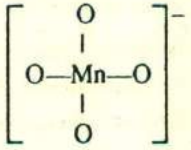
$$MnO_4^{-2}/MnO_4^- = 0.50 \text{ volts}$$

govern the reduction of Mn^{+7} to either Mn^{+4} or Mn^{+2} (K_2MnO_4 being unstable is changed to MnO_2 from Mn^{+6} to Mn^{+4}). The change depend upon the pH of the solution.

Free $HMnO_4$ in solution is obtained by the reaction of $Ba(MnO_4)_2$ with H_2SO_4 :

$$Ba(MnO_4)_2 + H_2SO_4 = BaSO_4 + 2HMnO_4$$

The structure of MnO_4^- ion is tetrahedral



Uses of $KMnO_4$: (1) As a reagent in quantitative analysis, (2) In organic reactions. (3) Dilute solution used in skin diseases (4) As an antibacterial reagent in water purification etc.

QUESTIONS AND PROBLEMS

1. (a) Write down the electronic formula of the oxy-ions of chlorine.
   (b) Discuss the reactions of Fluorine with (i) Alkalis, (ii) Carbon, (iii) Sulphur.
2. Write a note on Interhalogen compounds.
3. Discuss the properties of the members of group VIIA (The halogens). Give an account of the oxides and oxyacids of chlorine.
4. How would you prepare the following compounds? Give their reactions and tests :-
   Potassium chlorate and Potassium perchlorate.
5. How will you identify chloride, bromide and iodide in presence of each other?

6. Describe the preparation, properties and uses of bleaching powder. What chemical formula is assigned to it and why?
7. How is fluorine prepared? Compare its properties with those of other halogens.
8. Write a note on the commercial preparation of iodine. What reactions take place when iodine is treated with the following compounds :—
   (a) Caustic potash solution. (b) Chlorine, (c) Potassium chlorate
   (d) Hydrogen sulphide, (e) Sulphur dioxide.
9. Describe a method for preparing anhydrous hydrofluoric acid. How can you obtain fluorine from it? Discuss reactions to show that hydrofluoric acid and fluorides behave differently from other halides.
10. Explain, with examples, the behaviour of potassium permanganate as an oxidizing agent in acidic and alkaline medium.
11. How would you explain the highly reactive nature of alkali metals and halogens on the basis of their electronic structures?
12. Describe the preparation and uses of sodium hypochlorite.
13. Describe what happens when—(i) iodine reacts with a solution of $Na_2S_2O_3$, (ii) dry chlorine is passed over heated mixture of silica and charcoal.
14. Write a concise account of oxyacids of halogens.
15. Discuss the uses of $KMnO_4$ as a reagent in volumetric analysis.
16. Compare the chemistry of halogens and their important compounds.
17. Starting with pyrolusite how would you prepare $KMnO_4$? Discuss with examples, the oxidizing behaviour of $KMnO_4$ in acid, alkaline and neutral solutions.
18. Describe the preparation, properties and uses of :—
   (a) Potassium permanganate.
   (b) Hydroiodic acid.
   (c) Potassium chlorate,
   (d) Fluorine.
19. When a metal exhibits more than one oxidation states the halides of the lower states are the more ionic. Comment.
20. The ionic radii of F^- and O^{-2} are almost the same. What is the relationship between the two?
21. Fluorine is very reactive but HF is a weak acid. Discuss.
22. What is the reaction of glass with HF?
23. Discuss: Halogens are reactive elements.

24. On electrolysing a solution of NaCl, hydrogen gas is evolved at one electrode and Cl_2 at the other. Explain how NaOH is formed in the process.
25. Hydrogen fluoride attacks glass but hydrogen chloride does not. Does it prove that HF is a stronger acid than HCl?
26. Why is it necessary to prepare fluorine by electrolysis?
27. What is the difference between hydrochloric acid and hydrogen chloride?
28. HF is a liquid and has higher boiling point where other halogen acids are gases or liquids. Explain.
29. HF cannot be concentrated in aqueous solution. Explain
30. F shows only −1 oxidation states whereas other halogens show −1, +3, +4, +5 and +7 oxidation states. Explain with examples..
31. Explain why the compounds of fluorine with oxygen are fluorides of oxygen whereas those of other halogens are called oxides of halogen.
32. What are "freons" and "teflons"?
33. Write an account of the oxides and oxyacids of chlorine
34. Why is iodine more soluble in KI solution than in water
35. Describe the chemistry of interhalogen compounds.
36. Write a short note on basic iodine
37. Give the structures of oxyacids of chlorine.
38. What is bleaching powder? How does it react with KI in H_2SO_4? What is meant by "available chlorine" of bleaching powder ? How is this determined?
39. What is HTH? How is it prepared? Mention some uses of HTH.
40. Explain why interhalogen compounds are more reactive than halogen and are always diamagnetic
41. Discuss the structures of BrF_3 as IF_5
42. Discuss the structures of the following

    (a) ClO_2, ICl_2^-, ICl_4^-, Cl_2O

CHAPTER 23

IRON, COBALT AND NICKEL

(The Elements of Group VIII)

The elements of group VIII occupy the central positions of the Periodic Table and consists of three sets of triads. They belong to the first, second and third series of transition metals in which d-orbitals are being filled up. The atomic numbers, the outer electron orbitals and the oxidation states of group VIII metals are given in Table 23.1. This group has not been divided into sub-groups because of the proximity and electronic relationships.

Table 23.1. Group VIII metals

Elements	*At. No.*	*At. Wt.*	*Outer electron orbitals*	*Oxidation states Unstable ( )*
Fe	26	55.85	$3d^6\ 4s^2$	2, 3, (4), 6
Co	27	58.95	$3d^7\ 4s^2$	2, 3, 4
Ni	28	58.71	$3d^8\ 4s^2$	(1), 2, (3), 4
Ru	44	101.10	$4d^7\ 5s^1$	2, 3, 4, 6, 7, 8
Rh	45	102.91	$4d^8\ 5s^1$	(1), (2), 3, 4, (6)
Pd	46	106.40	$4d^{10}\ 5s^0$	(1), 2, —, 4, (6)
Os	76	190.20	$5d^6\ 7s^2$	(2), 3, 4, 6, (7), 8
Ir	77	192.20	$5d^9\ 7s^0$	(1), (2), 3, 4, 6
Pt	78	195.10	$5d^9\ 7s^1$	(1), 2, (3), 4, (6)

It is seen that the three sets of triads of group VIII elements have almost similar atomic weights. Similarity in many of the physical and chemical properties are also observed. But the increase in atomic numbers produces some alterations in the electron arrangements of the outer orbitals and consequently this affects the variable oxidation states. Among the triads the first series are more reactive and the reactivity decreases with the increase of atomic number to

a marked extent until the last triads, particularly Ir and Pt, are inert and noble metals. The six elements of the second and the third series of triads have similar properties and they occur in nature together in the form of alloys or in the free state. These six elements (Ru to Pt) are generally known as *Platinum group* of metals.

General Properties of Iron Group

1. The first series of triads—Fe, Co and Ni—show similar properties since the outer electron orbitals in each case consists of two 4s electrons outside a partially filled 3d orbital.

Fe (26)—$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

Co (27)—$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$

Ni (28)—$1s^2\ 2s^2\ 2p^2\ 3s^2\ 3p^6\ 3d^8\ 4s^2$

The three metals—Fe, Co and Ni are readily oxidized to +2 state by the removal of $4s^2$ electrons. Removal of a third electron from 3d orbital is easy for Fe because d^5 arrangement is more stable, and Fe readily forms the +3 state. But +3 state for cobalt is less stable and for Ni it is the least stable which occurs in some complexes only. Powerful oxidizing agents in alkaline solutions give +4 state for all the three elements and +6 state in the case of Fe as in ferrates, having FeO_4^{-2} ions. In each of the horizontal series of group VIII the tendency to lose electrons decreases as the nuclear charge increases

2. Trivalent cobalt is a powerful oxidizing agent and trivalent iron is less strong than cobalt. Co^{+3} is quite stable in the form of complexes, such as in $[Co(NH_3)_6]^{+3}$, $[Co(CN)_6]^{-3}$ etc. Ni^{+4} occurs in NiO_2.

3. Fe, Co and Ni have great tendency to form complex compounds which is due to the partially filled **d** electron orbitals. Fe and Co complexes are mostly octahedral having coordination number 6. Ni forms in addition to square planar and tetrahedral compounds having coordination number 4, a large number of octahedral complexes as well.

Physical properties : The metals Fe, Co and Ni have similar appearance in the free state. It is remarkable that not only they have similar

atomic weights but also similar melting points, density and other physical properties. Fe exists in four solid forms and Co and Ni have two modifications. The high oxidation states (6) in Fe, Co, Ni causes the bonds in the metals to be very strong and imparts valuable physical properties which are almost similar. They have also magnetic properties. The closeness of melting and boiling points of these metals indicate similarity in metallic bonding. Some of their physical properties are given in Table 23.2 for comparison.

Table 23.2 Physical properties of Fe, Co and Ni.

Properties	*Fe* 26	*Co* 27	*Ni* 28
Melting point (°C)	1540	1480	1450
Boiling point (°(C)	3000	2900	2900
Density (g/cm^3)	7.86	8.93	8.89
Ionization potential (ev)	7.83	7.70	7.69
Metallic radius (Å)	1.26,	1.25	1.24
Ionic radius M^{+2} (Å)	0.75	0.72	0.70
Oxidation potential M/M^{+2} (v)	0.44	0.28	0.25
Magnetic properties	Highly magnetic	Feebly magnetic	Feebly magnetic
Electronegativity	1.64	1.70	1.75

These metals have special technological importance due to the special properties which they possess. Apart from these the general reactions of Fe, Co and Ni have been summarized in Table 23.3 for comparison indicating the similarities in many of their properties.

IRON

Metallurgy of Iron

Occurrence : Iron is one of the most abundant elements found in the earth's crusts, meteors, rocks, minerals, soils, plants and animals. The haemoglobin of the blood contains iron which functions as oxygen carrier.

Table 23.3. Reactions of Fe, Co and Ni.

Reagents	*Fe*	*Co*	*Ni*	*Conditions of reactions*
Air (O_2)	Fe_3O_4, Fe_2O_3	Co_3O_4	NiO	500°C and above
Water (steam)	$Fe_3O_4 + H_2$	$CoO + H_2$	$NiO + H_2$	Red heat
Halogens	FeX_3, FeI_2	CoF_3, CoX_2	NiX_2	Generally at elevated temperature
Carbon	Fe_3C	Co_3C	Ni_3C	Above 1200°C
Sulphur	FeS	CoS	NiS	Heated
Carbon monoxide	$Fe(CO)_5$	$Co_2(CO)_8$	$Ni(CO)_4$	Below 100°C
NH_3	$Fe_2N + H_2$	$Co_4N_2 + H_2$	$Ni_4N_2 + H_2$	400—600°C (No direct reaction with N_2)
Conc. HNO_3	Passive	Passive	Passive	In other strong oxidizing agents also

Sources : The following are the important iron bearing ores :

Hematite—Fe_2O_3

Magnetite—Fe_3O_4

Limonite—$2Fe_2O_3.3H_2O$

Siderite—$FeCO_3$

The sulphide ore, *pyrites*, FeS_2, occurs as pale yellow crystals and looks like gold ; hence the name *fool's gold.* Pyrites is a quite abundant mineral of iron but only used for production of SO_2. The impure iron oxide residue is not generally used for the metallurgy of iron.

Metallurgical process for pig iron : The main operation for production of iron is based on the principle of the reduction of the iron oxide with carbon monoxide. The reduction is carried out in a furnace called *blast furnace.*

The iron ore used for the purpose is first washed, concentrated and then roasted in order to removes as much sulphur and phosphorus as possible. The roasting process removes water, decomposes carbonates to oxides and oxidizes

sulphides. The prepared oxide ore is mixed with sufficient limestone and coke and this mixture is fed into the blast furnace from the top with double cup and cone arrangements.

The blast furnace is made of steel and lined with fire bricks in the shape of a large cylindrical shaft about 100 feet high and 25 feet in diameter. Dry air under pressure preheated to about 500°C is blown in through the nozzles or *tuyeres* at the bottom part of the furnace. The bottom part also contains the outlet for the molten iron and an outlet to drain out the molten slag from the top of the molten metal. The illustration in Fig. 23—1 gives an outline of a diagrammatic

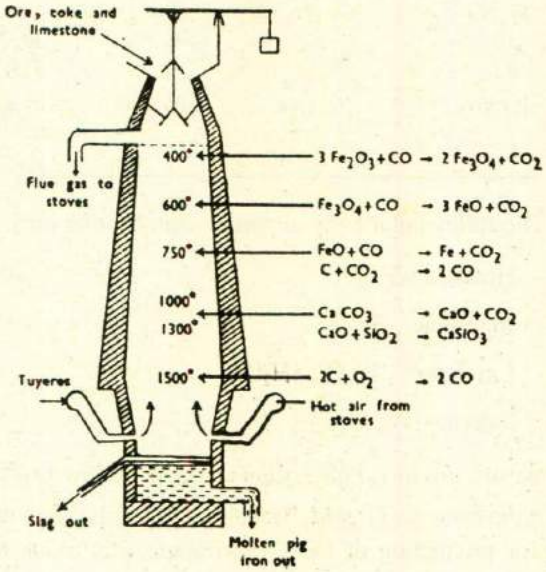


Fig. 23—1. Blast furnace for pig iron.

sketch of a blast furnace. The blast furnace has arrangements for continuous operations and produces pig iron in tons quantities.

The reactions taking place in the various regions of the blast furnace have been given in Fig. 23—1. The coke is first oxidized by the hot blast of air at the bottom to produce CO and CO_2 with the li ation of much heat upto 1500°C. The intense heat at this region liquefies the iron and the slag is formed at the

central region of the furnace due to the reduction by CO and decomposition of $CaCO_3$ to CaO and CO_2. The reduction of Fe_2O_3 by CO is a reversible process :

$$Fe_2O_3 + 3CO \rightleftharpoons 2Fe + 3CO_2$$

The excess of CO formed in the furnace shifts the equilibrium to the right. The flux used depends upon the impurities present in the ore. Limestone is used when sand is present and sand is added when limestone is the impurity. CaO forms the slag with SiO_2, i.e., $CaSiO_3$.

At the bottom the molten iron and the slag collect in two layers. The molten slag floats on top of the molten iron. The molten iron is withdrawn through the bottom tap hole and may be cast in the form of pigs known ads *Pig Iron*. The slag is often used in the manufacture of *Portland cement*.

The exhaust or flue gases which come out from the top of the blast furnace contain considerable amount of CO. This is mixed with air and burnt to preheat the air blast.

Pig iron and cast iron : The iron metal obtained from the blast furnace is called *Pig Iron*. It contains a number of impurities, such as 3—4% C together with Si, P, Mn and small amount of S. It is brittle and converted to cast iron and steel.

Cast Iron is obtained when pig iron is remelted and cooled. Rapid cooling of molten pig iron produces *White Cast Iron*. The white appearance is due to the chemical combination of C with Fe to form Fe_3C, known as *Cementite*, which is of light colour. It is brittle and hard. When pig iron is slowly cooled, the carbon separates as graphite and gives the iron a grey appearance. This is called *Grey Cast Iron* and is soft but tough.

Wrought iron : Wrought iron is a pure form of iron and is manufactured by melting pig iron with an excess of iron oxide which oxidizes out most of the impurities. Carbon and sulphur are expelled as CO_2 and SO_2. Si-and P-oxides react with Fe and Mn-oxides or with limestone which is sometimes added as flux to form slag. As the iron becomes pure its melting point rises and the metal collects in lumps which are removed. The operation is carried out in a reverberatory furnace.

Wrought iron is soft, malleable and ductile. It contains only 0.2% carbon. It has fibrous structure which is mainly due to thin films of slag between layers of pure iron.

It is used in the manufacture of articles which are subject to sudden stresses such as chains, anchors, bolts, frame-work etc. But now-a-days wrought iron has been displaced by *mild steel.*

Manufacture of Steel

The term *steel* is used for many different types of iron alloys with carbon. Iron which contains from 0.05 to 2% carbon and which is capable of being hardened by quenching is called *steel.* Other metals, such as Mn, Cr, Ni, W, Mo, V are added to produce different types of *alloy steels* for specific uses. Steel is made by various methods; the important methods are —(1) Bessemer Process and (2) Open-hearth Process.

(1) Bessemer Process : In this process a blast of air is blown through molten pig iron in a large oval-shaped vessel called *Bessemer converter.* The air blast enters through perforations at the bottom and oxidizes most of the impurities in the pig iron. Only a part of the carbon is oxidized. When Bessemer converter is lined with silica bricks, it is called the *Acid Bessemer Process.* This is applicable in the case of pig iron containing low percentages of S and P. The *acid* lining acts as a flux toward basic oxides produced during oxidation. A Basic Bessemer Process uses a *basic lining* of magnesia or lime for pig iron containing higher proportions of P and some amount of S. These impurities burn up to their oxides:

$$P_4 + 5O_2 = P_4O_{10}$$

$$S + O_2 = SO_2$$

After the first blast for about 15 minutes (during which period CO along with other impurities burns at the mouth of the converter) the desired composition of steel is adjusted by adding calculated quantities of carbon, manganese in the form of *spiegeleisen*, or other metals.

Bessemer steel is a low-grade steel and is used for steel frameworks for buildings, bridges and other constructional purposes.

(2) Open-hearth Process : In this process the pig iron is generally mixed with scrap iron, iron oxide and some limestone in a shallow hearth open at the top. The heat is supplied by a gas flame directly over the top surface. The iron ore and the rust on scrap iron which are parts of the charge help in the oxidation of the impurities. CO escapes, while the oxides of S and P combine with Fe_2O_3 and the basic oxides of the lining to form a slag which adds to the lining.

About 8-12 hours are required for the oxidation of the impurities :

$$3P_4 + 10\,Fe_2O_3 = 3P_4O_{10} + 20Fe$$

$$3S + 2Fe_2O_3 = 3SO_2 + 4Fe$$

When the desired carbon content is reached, the molten steel is run out into ladles. The capacity of a large furnace is about 500 tons of steel per charge. Some iron, low in sulphur and phosphorus, are made by open-hearth containing acid lining of silica. Desired quantities of other metals are added as in the case of Bessemer Process for special steel.

Open-hearth steel is high grade steel and uniform in quality. It is used for making girders, heavy rails, guns, armour plates, ship industries etc.

(3) Duplex Process : High-grade steel is manufactured by combining operations of acid Bessemer converter and basic open hearth process. Pig iron is first processed in acid bessemer converter and then transferred to basic Open-Hearth. Steel of very low phosphorus content is obtained.

(4) Other Processes: Other high-grade steels are made in small quantity for specific purposes. These are: (a) *Crucible Steel* produced by heating wrought iron with graphite in small crucibles. (b) *Electrothermal steels* are high-grade steel and alloy steel made in a furnace heated electrically at rigidly controlled temperatures. Both crucible steel and electrical steel are used as tool-steel. (c) *Case-hardened steel* is made by heating low-carbon steel in closed containers with powdered carbon followed by quenching in oil. The carbon reacts on the surface and forms cementite, Fe_3C. Such steel is very hard on the surface and tough in the interior. This is used for making axles, auto-parts, machine parts, anvil etc. (d) *Nitriding steel* is surface-coated by case-hardening process with ammonia or

nitrogen compounds. A very hard surface of nitride of Fe or alloy metal is formed.

Heat treatment of steel : Various methods of heat-treating produce steel of different qualities. Such processes are : *Annealing*, steel heated to redness and allowed to cool slowly. *Quenching*, steel heated to redness and rapidly cooled in water or oil. *Tempering*, steel held at a fixed temperature for sometime before cooling. These treatments produce different sizes of interlacing crystals.

Alloy steel : Many important special steels are manufactured by adding metals other than carbon. Steel of widely varying properties are made by appropriate choice of the number and percentages of these elements. Some of these are given in Table 23.4.

Table 23.4 Comparison of some alloy steels.

Alloy	*Composition*	*Properties*	*Use*
Mn-steel	10—18% Mn	Hard, tough, resistant to wear	Rails, armour plates, ball crushers
Si-steel	1—5% Si	Hard, strong, highly magnetic	Magnets
Duriron	12—15% Si	Corrosion resistant	Pipes, sheets
Invar	36% Ni	Low co-efficient of expansion	Pendulum rods, meter scale, measuring instruments
Stainless steel	14—18% Cr 7—9% Ni	Corrosion resistant	Cutlery, machine parts and in industry
High-speed steel	14—20% W or 6—12% Mo	Retain temper at high temperature	High speed cutting tools

Rusting of Iron : Pure iron is silvery white but when left in moist air it is covered with reddish deposit commonly known as *rusting of iron*. It undergoes the process of *corrosion* (rusting) which is favoured by (i) impurities in water, (ii) impurities in iron, (iii) presence of moist air, (iv) presence of dissolved oxygen and CO_2 in water, (v) higher temperature than the normal.

Thus pure iron will not rust in pure water and pure air. Rusting has been explained on the basis of setting up of small galvanic or electrical cells in which iron acts as anode and an impurity, particularly of less active metals, e.g., Cu,

Pb, Sn etc., acts as cathode and the impure water serves as the electrolyte. Dissolved oxygen removes the hydrogen formed during the process and accelerates corrosion. Presence of more active metal, such as Zn, retards corrosion. Ferrous iron combines with hydroxide ion of the electrolytic solution forming $Fe(OH)_2$ which is readily oxidized in presence of air to $Fe_2O_3.H_2O$ which is the composition of *iron rust*.

Several methods have been devised to prevent or retard iron rust. Some of these are—(i) coating the surface with paint, grease, asphalt etc., (ii) coating with other metals such as Zn, Ni, Al etc., (iii) coating with enamels, (iv) coating with an adherent oxide such as Pb_3O_4, (v) alloying to produce non-rusting materials, (vi) cathodic protection.

Passivity of Iron : Iron dissolves in HCl and dilute H_2SO_4 to form Fe^{+2} ions and H_2. Cold concentrated HNO_3 renders the iron inactive. Such treated iron does not react with dilute acids and does not displace Cu from $CuSO_4$ solution. This state of iron is called *passivity* and the iron itself is called *passive iron*. Passivity can be produced by means of compounds, such as $K_2Cr_2O_7$, H_2O_2, $HClO_3$ and HIO_3 and other oxidizing agents in solutions. Passivity has been explained from various points of views. One view is the formation of Fe_3O_4 film on the surface. Passivity of iron can be removed by scratching and polishing the surface, by treating with halogens, by heating in presence of H_2 and by anodic electrolysis in salt solutions.

Compounds of Iron

Oxides and hydroxides of Fe : Iron forms three oxides having composition FeO, Fe_2O_3 and Fe_3O_4. FeO is obtained by thermal decomposition of ferrous oxalate, FeC_2O_4, or by reduction of Fe_2O_3 in hydrogen at 300°C:

$$FeC_2O_4 = FeO + CO + CO_2$$

$$Fe_2O_3 + H_2 = 2FeO + H_2O$$

FeO is unstable and has the structure like that of NaCl. On standing it is converted to a mixture of Fe and Fe_3O_4 (disproportionation):

$$4FeO = Fe + Fe_3O_4$$

FeO is also a non-stoichiometric compound in which the composition does not exactly correspond to FeO.

$Fe(OH)_2$ is formed when a ferrous salts solution is treated with alkali hydroxide. It is a white precipitate when freshly formed, but quickly turns green and reddish brown due to oxidation of Fe^{+2} to Fe^{+3}:

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$$

Fe_2O_3 is obtained by igniting $Fe(OH)_3$ or by roasting pyrites, FeS_2 in the air. It is a red powder and is used as paints under the name of red oxide of iron, *rouge* and also *Venetian red.* Fe^{+3} salt solutions give precipitate of $Fe(OH)_3$ or hydrated iron oxide, $FeO.xH_2O$, on treatment with alkali solution. Fe_3O_4 or magnetic oxide of iron is actually a mixed oxide containing $FeO.Fe_2O_3$. The magnetic oxide of iron Fe_3O_4, is obtained when Fe is heated strongly in air. This is the most stable form of iron oxide at high temperature. Fe_3O_4 is also $FeFe_2O_4$ possessing the spinel structure.

Ferrous compounds : The two most familiar ferrous salts are sulphates, $FeSO_4.7H_2O$ and $FeSO_4.(NH_4)_2SO_4.6H_2O$ (*Mohr's salt*). These are used as laboratory reagents. Mohr's salt is a double salt and is prepared by crystallising from an equimolar solution of $(NH_4)_2SO_4$ and $FeSO_4$. Unlike $FeSO_4$ which is readily hydrolysed in aqueous solutions and oxidized in air, Mohr's salt does not undergo quick hydrolysis and oxidation in air.

Fenton's Reagent : A solution of $FeSO_4$ and H_2O_2 (mixture) is called Fenton's Reagent and is used to catalyse the conversion of acrylonitrile $CH_2 = CH_2 - CN$ to its polymer. The reaction is

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^\circ + OH^-.$$

The OH° radical functions for polymerisation.

Complex compounds of iron (II)

Fe^{+2} salts form complexes, such as with KCN, to form potassium hexacyanoferrate i.e, potassium ferrocyanide, $K_4Fe(CN)_6$. This is the most stable complex of ferrous iron. This is obtained by adding excess of KCN to a ferrous salt solution and recrystallising. $K_4Fe(CN)_6$. is used as a reagent for ferric iron forming *Prussian blue* :

$$Fe^{+2} + 6CN^- = [Fe(CN)_6]^{-4}$$

$$FeCl_3 + K_4[Fe(CN)_6] = KFeFe(CN)_6 + 3KCl$$

$$4FeCl_3 + 3K_4[Fe(CN)_6 = Fe_4[Fe(CN)_6]_3 + 12KCl$$

$K_4Fe(CN)_6$ is used as a reagent for other metals, e. g., Cu, Zn etc. $K_4Fe(CN)_6$ forms the nitroderivative with NO_2^- ion. This on treatment with acid gives the *nitroprusside* ion :

$$Na_4[Fe(CN)_5NO_2] + 2HCl = \underset{\text{Na-nitroprusside}}{Na_2[Fe(CN)_5NO]} + H_2O + 2NaCl$$

Na-nitroprusside forms a thionitro-complex with sulphide forming an intense blue-violet solution used as a delicate test for sulphides. The reaction takes place with HS^- ion :

$$[Fe(CN)_5NO]^{-2} + HS^- \rightarrow \left[Fe(CN)_5N\begin{matrix}O\\ \diagup\\ \diagdown\\ S\end{matrix}\right]^{-4}$$

NO may be present as NO^+ and Fe as Fe^{+2} or NO is neutral and Fe is present as Fe^{+3}. The composition is, therefore, uncertain.

Ferric compounds : $FeCl_3$, $Fe_2(SO_4)_3$, $Fe(NO_3)_3$, $Fe(OH)_3$ and $FePO_4$ etc. are quite familiar compounds. The colours of these compounds differ mainly due to hydrated or dehydrated state. Fe^{+3} ion is smaller in size and has greater charge than Fe^{+2} and, therefore, the compounds of Fe^{+3} are more acidic. Ferric salts are, therefore, greatly hydrolysed in aqueous solution and resemble Al^{+3} in many respects.

Anhydrous $FeCl_3$ is obtained by heating Fe in Cl_2 gas. The composition corresponds to Fe_2Cl_6. Hydrated $FeCl_3.6H_2O$ solutions contain undefined $FeCl_3$ complexes because its solution is more intensely coloured than $Fe(NO_3)_3$ or $Fe_2(SO_4)_3$ solutions :

Complex Compounds of iron (III)

Excess KCN forms $K_3Fe(CN)_6$ with ferric salt solutions. $K_3Fe(CN)_6$, i.e., potassium hexacyanoferrate (III) or potassium ferricyanide gives blue-coloured precipitate or solution with Fe^{+2} salt solution. The blue compound in this case having $Fe_3[Fe(CN)_6]_2$. H_2O is known as *Turnbull's blue* and is used as pigment. Acid insoluble Turnbull's blue was considered to be formed by the reaction :

$$3FeSO_4 + 2K_3Fe(CN)_6 \rightarrow Fe_3[Fe(CN)_6]_2 + 3K_2SO_4$$

The other compound known as *Prussian blue* soluble in acids is considered to be formed by the reaction :

$$4FeCl_3 + 3K_4Fe(CN)_6 \rightarrow Fe_4[Fe(CN_6]_3 + 12KCl$$

The commercial Prussian blue as well as Turnbull's blue do not exactly correspond in their compositions to the above formula. Both the compounds contain combined water. Both the compounds are decomposed by alkali. The colour of these compounds depends on the conditions of their formation. It is now generally believed that Turnbull's blue (ferrous ferricyanide) and Prussian blue (ferric ferrocyanide) having blue colours are potassium ferric ferrocyanide $KFe[Fe(CN)_6].H_2O$.

Ferric Ammonium Alum : $Fe_2(SO_4)_3.(NH_4)_2SO_4.24\ H_2O$ is obtained by oxidation of Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, with HNO_3 with additional $FeSO_4.7H_2O$ and H_2SO_4. The solution after complete oxidation and evaporation gives crystalline product. The iron alum forms large reddish octahedral crystals.

SCN^- ions produce blood-red coloured solution of $[Fe(SCN)_6]^{-3}$ ions with Fe^{+3} ion. This is used to detect the presence of Fe^{+3} in solution.

Cl_2 in alkaline solution converts $Fe(OH)_3$ to ferrate, FeO_4^{-2} ion containing Fe^{+6}. Potassium ferrate is formed by the reactions :

$$3Cl_2 + 2Fe(OH)_3 + 10KOH = 2K_2FeO_4 + 6KCl + 8H_2O$$

Ferrate ion, FeO_4^{-2}, is an extremely powerful oxidizing agent in acid solution and like SO_4^{-2}, CrO_4^{-2},MnO_4^{-2} ions form insoluble barium ferrate, $BaFeO_4$.

COBALT

Sources: The following are the important cobalt bearing ores :

Cobaltite—CoAsS (cobalt glance)

Smaltite—$CoAs_2$

Extraction : The metallurgy of cobalt involves separation from Cu, Ni, Fe etc. and then the conversion of the ore to CoO to Co_3O_4. These oxides on reduction with Al gives metallic Co by alumino thermit process :

$$3Co_3O_4 + 8Al = 9Co + 4Al_2O_3$$

Purification of cobalt is made by electrolytic process. Co is used as a catalyst in the Fischer–Tropsch Process for the hydrogenation of CO to various hydrocarbons and for oxidation of NH_3. When heated in air Co_3O_4 is formed.

Compounds of cobalt (II) : Soluble salts of Co^{+2}, such as chloride, nitrate, sulphate, acetate etc. are of pink colour in the hydrated condition formulated as $Co(H_2O)_6^{+2}$. When dehydrated the deep blue colour of the anhydrous salts appears. The hydration or the dehydration follows the equilibrium:

$$\underset{\text{pink}}{2[Co(H_2O)_6]\,Cl_2} \overset{\overset{-H_2O}{\rightleftharpoons}}{\underset{+H_2O}{}} \underset{\text{blue}}{Co[CoCl_4]} + 12H_2O$$

Co on both sides of the equation has Co^{+2} oxidation states.

$Co(OH)_2$ is first precipitated by adding caustic alkali to a Co^{+2}-salt solution but soon becomes black due to the formation of hydrated cobaltic oxide, Co_2O_3 :

$$4Co(OH)_2 + 2H_2O + O_2 \rightarrow 4Co(OH)_3$$

In concentrated NH_4OH, the precipitate of $Co(OH)_2$ dissolves forming hexaminocobalt(II) hydroxide, $[Co(NH_3)_6](OH)_2$. The complex ion, $[Co(NH_3)_6]^{+2}$, is readily oxidized in air to form $[Co(NH_3)_6]^{+3}$ complexes :

$$4[Co(NH_3)_6]^{+2} + O_2 + 2H_2O \rightarrow 4[Co(NH_3)_6]^{+3} + 4OH^-$$

$Co(NH_3)_6\,Cl_3$ is prepared by adding NH_4Cl and NH_4OH to a solution of $CoCl_2$ and passing a current of air through the dark red solution. The rose coloured precipitate of $[Co(NH_3)_5\,H_2O]Cl_3$ with HCl gives $[Co(NH_3)_6]Cl_3$ as orange coloured crystals.

Cobalt nitrate, $Co(NO_3)_2.6H_2O$, is obtained by dissolving CoO or $CoCO_3$ in HNO_3. The anhydrous salt is made by the action of NO_2 on heated salts of Co^{+2}. Cobalt nitrate solution is used in the analytical tests for Zn, Al, PO_4^{-3} etc. by heating to incandescence with a drop or two of cobalt nitrate solution on a piece of charcoal.

Al	—	$CoO.\,Al_2O_3$	Blue	Thenard's blue
Zn	—	$CoO.\,ZnO$	Green	Rinman's green
PO_4^{-3}	—	$CoPO_4$	Blue	—

Sodium cobaltinitrite, $Na_3[Co(NO_2)_6]$, is prepared from Co^{+2} salt solutions by adding $NaNO_2$ in presence of acetic acid (aerial oxidation) :

$$2CoCl_2 + 14NaNO_2 + 4CH_3COOH = 2Na_3[Co(NO_2)_6] + 4CH_3COONa + 4NaCl + 2H_2O + 2NO$$

This is used as a reagent for K^+ ion, the insoluble yellow $K_3[Co(NO_2)_6]$ being precipitated out.

It will be seen that the cyanide complexes of Co^{+2} and Co^{+3} ions formed by adding excess of KCN to a solution of Co^{+2} ions might have the compositions $K_4Co(CN)_6$ and $K_3Co(CN)_6$ respectively. But $K_4Co(CN)_6$ has one electron in an unstable position beyond the inert gas core or one extra electron at a higher energy level than that required for d^2sp^3 hybrid bond formation. Hence this acts as a powerful reducing agent by easily giving up the single electron. But it is now known that the complex is $K_3[Co(CN)_5 H_2O]$ and not $K_4[Co(CN)_6]$.

Cobalt forms quite a large number of complexes with many types of ligands (coordinating groups).

NICKEL

Occurrence : Nickel occurs with iron meteorites in the form of an alloy. Metallic Ni and Fe constitute most of the core of the earth. Ores of nickel always contain Co and other metals. The commercial sources of nickel ores are :

Sources : Nickelite—NiAs (Kupfer nickel)

Linnacite—$(Fe, Co, Ni)_3S$

Nickel glance—NiAsS

Pentalandite—(FeNi)S

Pentalandite, (FeNi)S, is abundantly found is Sudbury of Canada, which is the world's chief supplier of nickel.

Metallurgy of Nickel

Large amount of impurities and the presence of Fe, Co, Cu etc. make it difficult for the production of pure Ni. The following steps are involved in the metallurgical operations of Ni.

(1) Concentration of the ore : This is usually done by selective froth floatation by which means NiS, CoS and FeS are separated.

(2) Roasting : The separated NiS is roasted to produce NiO which is generally mixed with some FeO and CuO together with unconverted FeS, CoS, NiS etc.

(3) Smelting : The roasted ore is smelted with coke, sand and some limestone to remove some Fe as the slag, $FeSiO_3$. The product is called *Matte*.

(4) Bessemerization : The matte is bessemerized in a Bessemer converter with silica as flux and iron is almost completely removed. The product consists of NiS, CoS and some NiO. The bessemerized matte is further roasted to convert the sulphides to oxides. Any CuO left is removed by leaching out with H_2SO_4.

(5) Production of Nickel : (a) Mond's Process and (b) Orford Process.

(a) Mond's Process : Nickel forms a volatile compound with CO giving nickel carbonyl, $Ni(CO)_4$. When $Ni(CO)_4$, which is a volatile liquid, is heated to 180°C in the vapour state, it is decomposed to give pure Ni and CO.

The impure nickel oxide is heated to 300°C in a current of water gas (H_2 + CO). NiO is reduced to Ni but impurities remain as oxides. The reduced product is treated with carbon monoxide, CO, in a volatilizer at about 60°C. Volatile $Ni(CO)_4$ is formed which is passed through the decomposer at 180°C by means of sweeping with water gas. $Ni(CO)_4$ is decomposed to give nickel :

$$Ni(CO)_4 = Ni + 4CO$$

CO released is used over again.

This process may be described by the flow-sheet. (see page 672)

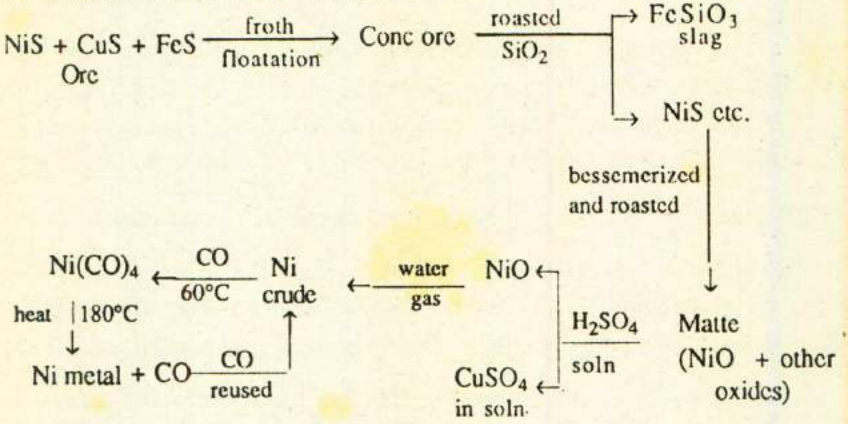
(b) Orford Process : The Bessemer matte consisting mainly of NiS and CuS is fused with carbon and sodium sulphate. Na_2S is formed which in the molten condition dissolves both CuS and NiS. But the solution of NiS in molten Na_2S has greater specific gravity than that of CuS in molten Na_2S and they separate in two layers. The bottom layer consisting of NiS in Na_2S which is separated, cooled and Na_2S is leached out by washing with water.

(CuS + NiS) matte + $2NaHSO_4$ + 8C = CuS + NiS + Na_2S + H_2S + 8CO.

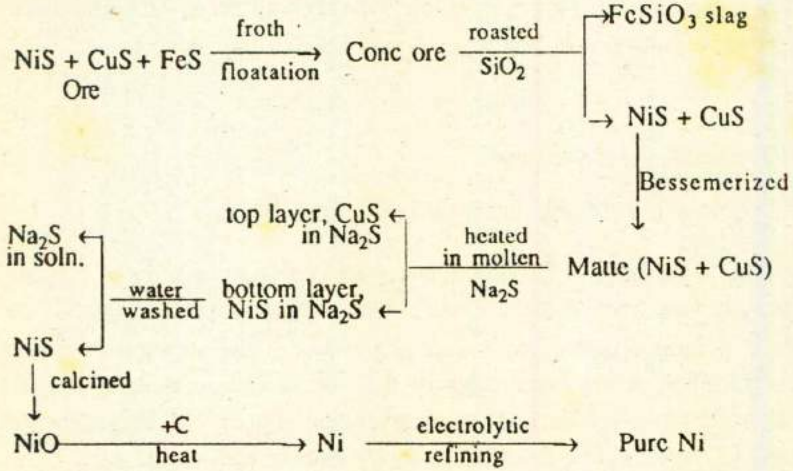
The NiS produced may contain small quantity of CuS. This is removed by chloridizing the copper when heated with NaCl. $CuCl_2$ formed is removed by washing with water. NiS is then calcined to form NiO which on heating with carbon gives Ni:

$$NiO + C = Ni + CO$$

Flow-sheet for Mond's Process :



Flow-sheet for Orford Process :



Refining of nickel : Curde nickel is cast into anodes and refined electrolytically in a $NiSO_4$ or $NiSO_4.(NH_4)_2SO_4$ bath having strips of pure nickel as cathodes on which pure nickel is deposited during electrolysis. Noble metals, specially platinum, are recovered from the anode mud which collect in the anode region at the bottom of the cell.

Uses of Nickel : (1) In a finely divided form (known as Raney nickel) it is used as a catalyst in the hydrogenation of oils and fats. (2) For making crucibles and laboratory apparatus. (3) Nickel used for electroplating. (4) For making special alloys, such as the following :—

(a) Nichrome—Ni(60%), Fe(25%), Cr(15%), used for resistance heaters.

(b) German silver—Cu (55%), Ni (20%), Zn (15%), used for cutlery and household utensils.

(c) Monel metal—Cu (60%), Ni(40%), used for both industrial and household wares.

(d) Invar—Ni (35%), steel, used for pendulums of clocks.

(e) Alnico, (Al-Ni-Co-Fe alloy) and other alloys of special use.

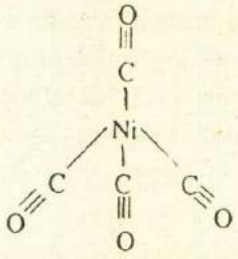
Nickel plating : Because of its hardness, resistance to corrosion and high reflectivity when polished, nickel is widely used in plating of iron, steel, copper etc. The article to be plated is first given a coat of thin film of copper. The electrolytic bath is a mixture of $NiSO_4$ or $NiSO_4.(NH_4)_2SO_4$ containing only small concentration of Ni. At the cathode Ni is deposited while an equivalent amount goes into solution from the Ni anode. The pH of the electrolyte is controlled at about 6.5 with the help of H_3BO_3. Bright deposits are obtained by adding some glucose or cadmium salt in the bath which is operated at about 50°C with a current density of 2.5 amp/decimeter^2.

Compounds of Nickel

The divalent form of Ni is the most important oxidation state. Most of the anhydrous Ni salts are yellow but in aqueous solution they are all green due to the formation of $[Ni(H_2O)_6]^{+2}$ ions.

NiO is obtained by heating $NiCO_3$ and the other divalent salts are prepared by the reactions of NiO, $Ni(OH)_2$ or $NiCO_3$ with the appropriate acids and crystallisation.

It is formed as a colourless volatile liquid when CO is passed over finely divided Ni. It readily decomposes at higher temperatures depositing pure Ni (basis of Mond's Process). The oxidation state of Ni in $Ni(CO)_4$ is zero. $Ni(CO)_4$ has the tetrahedral structure having Ni at the centre and the four CO at the corners of the tetrahedron. Ni uses sp^3 bonds in $Ni(CO)_4$.



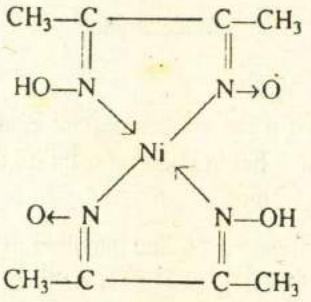
Tetrahedral structure of $Ni(CO)_4$

Ni-salts in presence of NH_4Cl and excess NH_4OH produce complex hexamine nickel(II) compounds. $Ni(OH)_2$ first formed goes into solution in excess giving deep blue solutions.

Complexes of $[Ni(CN)_4]^{-2}$ and chelates of organic ligands are square planar. Ni-chelates of 1,2-dioximes are of deep red colour and used for both specific identification and quantitative determination of nickel. Thus dimethyl glyoxime,

$$\begin{array}{l} CH_3—C=NOH \\ \quad\quad | \\ CH_3—C=NOH \end{array}$$

gives a red coloured precipitate with Ni^{+2} salt solutions, soluble in acid but insoluble in ammonia solution and is a specific test for Ni :



Ni-dimethyl glyoxime complex

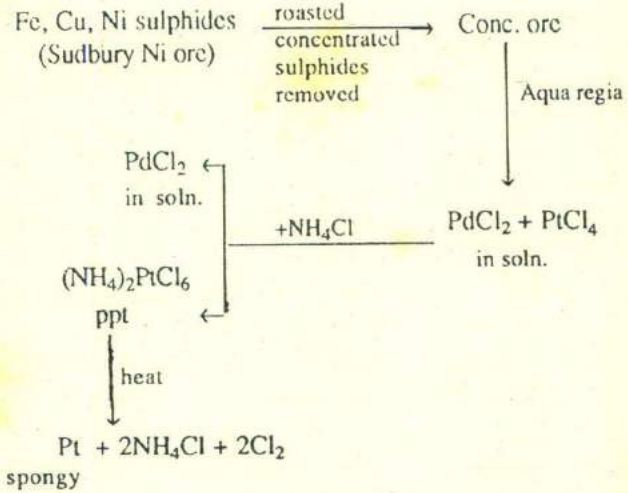
Such complexes are known as chelates or inner complex salts, because they are electrically neutral and do not conduct electricity in solution. Cobalt does not form such complexes with dimethyl glyoxime. Hence the formation of red precipitate with dimethyl glyoxime is a means to identify Ni in presence of Co. This is also used in quantitative method for the determination of nickel.

The other triads of Group VIII elements are Ru, Rh, Pd and Os, Ir, Pt. A brief chemistry of Pt is described.

Platinum

Occurrence : Pt occurs in native form with gold and also along with Cu, Fe, Ni and other Pt-metals. Ural mountains in Russia is the main source. Pt is generally extracted from Sudbury Ni-ore also.

Extraction :



Spongy platinum : It is gray porous form of platinum. It has great surface activity and used for absorption of gases.

Platinum black : It is obtained by the reaction of platinic chloride with formic acid. Pt black is also used for absorption of hydrogen and used in reduction and a catalyst. It is also called platinized platinum.

Platinized asbestos : Asbestos soaked in platinic chloride in presence of HCl and NH_4Cl when heated gives the Pt metal in reduced from and deposited on the asbestos. This is used as a catalyst.

Platinum and Platinum compounds are used in (a) making scientific instruments, (b) as catalyst in contact process for H_2SO_4 and manufacture of HNO_3, (c) for formaldehyde, (d) hydrogenation industries, (e) in jewellery, (f) in dentistry and (g) in printing and toning photography.

QUESTIONS AND PROBLEMS

1. Describe the metallurgy of nickel from its ores. Describe its properties and its alloys. Explain the method of separating nickel from cobalt.
2. Write a note with the reactions involved on the Passivity and the Rusting of iron.
3. Describe any two important methods of preparing high-grade steel from pig iron. Mention a few special steels and their chief uses.
4. Give an account of the metallurgy of iron. Briefly explain the difference between cast iron, wrought iron and steel.
5. What are the important uses of iron? Discuss the chemical reactions occurring in the blast furnace. How is cast iron converted into steel?
6. What are the chief sources of nickel? How is pure nickel obtained from its ores? Describe the important uses of nickel.
7. (a) Describe the process of conversion of pig iron into steel by the Open-hearth Process. Discuss the chemistry of the reactions involved.
   (b) How will you compare Open-hearth Process with that of Bessemer Process.
   (c) What part do Ni and Cr play in the preparation of steel alloys?
8. Give a brief account of the metallurgy of nickel by Mond's Process. Mention some of the important alloys of nickel and mention their uses. Describe a method for the determination of nickel in a sample.
9. Describe the preparation, properties and the uses of following :—
   (a) Mohr's salt ;
   (b) Ferrochrome;
   (c) Nickel carbonyl.
10. What are iron, steel and pig iron? Discuss the principal process of production of pig iron and its subsequent conversion to steel by the Bessemer Process.
11. Compare the physical and chemical properties of the metals Fe, Co, and Ni and their simple compounds.

12. (a) Describe briefly the two compounds whose anions contain a metal.
    (b) Explain why $[Co(H_2O)_6]^{-2}$ is pink whilst $[CoCl_4]^{-2}$ is blue.
    (b) Name two alloys of nickel and mention their special properties.
    (c) How would you detect nickel in solutions containing cobalt and manganese?
13. Discuss the chemistry underlying the process of production of pig iron and its subsequent conversion to steel by the Bessemer Process.
14. How is nickel extracted from its sulphide ores? Mention two uses of nickel. How would you detect nickel in presence of cobalt in a mixture of their salts?
15. Give brief descriptions of metallurgical process for the production of pig iron.
16. Discuss briefly how pig iron can be converted into steel.
17. (a) Describe briefly the metallurgy of iron. (b) What is stainless steel? (c) Discuss the oxidation states of iron. (d) What is the difference between wrought iron and steel?
18. What is the difference between pig iron, white cast iron, gray cast iron, wrought iron and mild steel.
19. What are the raw materials for the production of steel by the Open-Hearth Process? Indicate the chemical reactions. How would you analyse the purity of iron in a sample of mild steel rod?
20. Explain passivity and rusting of iron.
21. What happen when NH_4OH and NH_4Cl is added to a solution of $CoCl_2$ in water?
22. Explain why Co^{+2} is stable in presence of water but is oxidized to Co^{+3} in presence of NH_4OH.
23. Discuss the relative facilities of plating with nickel and chromium.
24. Fe^{+3} gives blood-red colouration with NH_4CNS solution. What is the reaction?
25. How would you test for Fe^{+3} in a sample of Mohr's salt?
26. Write the geometrical figures of $[FeCl_5H_2O]^{-2}$, $[Co(CN)_5H_2O]^{-2}$ and $[Ni(CN)_4]^{-2}$
27. Why a piece of iron is attracted by magnet but zinc is not?
28. Describe the extraction of platinum.

CHAPTER 24

COMPLEX COMPOUNDS

(Coordination Chemistry)

A very large number of chemical compounds exist which appear to be composed of two or more compounds which are capable of independent existence and are themselves well-defined compounds. It was rather difficult to explain on the basis of classical theory of valency as to why such complex compounds are formed. For instance, compounds having the compositions $CuSO_4.5H_2O$; $K_2SO_4.Al_2(SO_4)_3.24H_2O$; $CoCl_3.6NH_3$; K_2PtCl_4; $K_4Fe(CN)_6$ etc. have real existence but could not be represented structurally on the basis of the classical concept of valency. For this reason, such compound used to be called as *molecular compounds* in which it was supposed that the component molecules were held together by some unknown forces. The molecular compounds were also referred to as *addition compounds*. Such compounds differ widely in their stability and their properties.

Let us consider the following compounds as regards stability :—

1. In $Na_2CO_3.10H_2O$ the water molecules are very loosely held and 9 molecules are lost on exposure to air. From $CuSO_4.5H_2O$ the water molecules are not so easily lost but only on strong heating. $CuSO_4$ is colourless whereas $CuSO_4.5H_2O$ is blue. These are generally classified as *hydrated compounds or hydrates*. The smaller the size of the cation, the lesser is the number of H_2O molecules in the hydrates. Thus $BeCl_2$ contains $4H_2O$ and $AlCl_3$ contains $6H_2O$. In hydrates some H_2O are combined with the cations and some with anions. Thus in $CuSO_4.5H_2O$ we have $4H_2O$ combined to Cu^{+2} and one H_2O to SO_4^{-2} ions. Similarly, in $MgSO_4.7H_2O$ we have $6H_2O$ combined to Mg^{+2} and one H_2O to SO_4^{-2} ions.

2. $K_2SO_4.Al_2(SO_4)_3 .24H_2O$ (alum) exists in the solid state as a single compound but on dissolution in water, all the ions (K^+, Al^{+3} and SO_4^{-2}) can be detected due to complete dissociation. Complex compounds of this type are generally called *double salts*.

3. There are compounds such as $K_2[Cd(CN)_4]$ which are reversibly dissociated into all the ions present in the molecule :

$$K_2[Cd(CN)_4] \rightleftharpoons 2K^+ + [Cd(CN)_4]^{-2}$$

$$\downarrow\uparrow$$

$$Cd^{+2} + CN^-$$

But the copper complex, $K_2[Cu(CN)_4]$, is not dissociated as in the case of $K_2[Cd(CN)_4]$, but only to the following ionic species :

$$K_2[Cu(CN)_4] \rightleftharpoons 2K^+ + [Cu(CN)_4]^{-2}$$

It is for this reason that Cd can be precipitated from $K_2[Cd(CN)_4]$ solution by H_2S as CdS but not copper from $K_2[Cu(CN)_4]$ solution.

Again, $K_3[Fe(CN)_6]$ in aqueous solution does not give tests for either Fe^{+3} or for CN^-. Similarly, in the compound $Co(NH_3)_6Cl_3$, heating with H_2SO_4 does not remove ammonia but 3 molecules of HCl are lost per molecule of $Co(NH_3)_6Cl_3$ and also cobalt does not respond to ordinary tests. But from $Co(NH_3)_6Cl_2$ ammonia is removed quite easily.

$$2[Co(NH_3)_6]\,Cl_3 + 3H_2SO_4 \longrightarrow [Co(NH_3)_6]_2(SO_4)_3 + 6HCl$$

$$[Co(NH_3)_6]Cl_2 \longrightarrow CoCl_2 + 6NH_3$$

Thus $K_3Fe(CN)_6$ and $Co(NH_3)_6Cl_3$ belong to the group known as *True Penetration Complexes*. Those complex compounds which are reversibly dissociated in solution into their components are known as Normal Complexes, such as $K_2Cd(CN)_4$ and $Co(NH_3)_6Cl_2$. Thus we can classify complex compounds according to their stability into four groups :—

1. Hydrates and related compounds ;

2. Double Salts ;

3. Normal Complexes ;
4. True Complexes.

It is evident that actually there is no fundamental difference between these complex compounds. Only the degrees of complexity and stability either depending on temperature or hydrolytic decompositions indicate different modes of combinations.

Complex compounds are chemical substances formed by the combination of components which are capable of independent existence.

Complex compounds are also known as coordination compounds.

The nomenclature of coordination compounds is derived from the electronic theory of the formation of coordination bond in which donation of a lone pair of electrons occur from one molecule or ion to another but are coshared between the donor and acceptor.

$$H_3N\overset{\bullet}{\underset{\bullet}{:}} + H^+ \longrightarrow H_3N\overset{\bullet}{\underset{\bullet}{:}}H^+ \longrightarrow NH_4^+$$

$$H_3N\overset{\bullet}{\underset{\bullet}{:}} + BF_3 \longrightarrow H_3N\overset{\bullet}{\underset{\bullet}{:}}BF_3 \longrightarrow NH_3BF_3$$

When a simple ion combines with one or more other ions or with one or more neutral molecules to form a new ion it is called a Complex Ion. Thus,

$[Co(NH_3)_6]^{+3}$, $[Cu(CN)_4]^{-2}$, $[Fe(CN)_6]^{-3}$

$[Cu(H_2O)_4]^{+2}$ etc. are complex ions.

Thus complex compounds contain complex ions which differ in their stabilities. The stability of complex ions is determined by their *dissociation* in solution at the equilibrium conditions. Thus :

$$Cu(CN)_4^{-2} \overset{Ki}{\rightleftharpoons} Cu^{+2} + 4CN^-$$

$$Cd(CN)_4^{-2} \overset{Ki}{\rightleftharpoons} Cd^{+2} + 4CN^-$$

The equilibrium constants also known as the instability constants of the complexes are give by the equation :

$$Ki = \frac{[Cu^{+2}][CN^-]^4}{[Cu(CN)_4^{-2}]} \qquad Ki = \frac{[Cd^{+2}][CN^-]^4}{[Cu(CN)_4^{-2}]}$$

Conversely, the *stability constants* Ks indicate the *formation* of the complex compounds :

$$Ks = \frac{[Cu(CN)_4^{-2}]}{[Cu^{+2}][CN^-]^4}$$

N.B. The terms in square brackets refer to the concentrations of the ionic species raised to the appropriate power. The concentration of water being taken as constant.

If the concentration of CN^- ions is large, naturally the complex ions is unstable and instability constant K*i* will be very large. Actually this happens in the case of $K_2[Cd(CN)_4]$ complex whereas in the case of $K_2[Cu(CN)_4]$ low value of $[CN^-]$ ion gives low result for the instability constant and, therefore, copper complex is more stable than the cadmium complex. In other words, the stability constant of the copper complex has a much higher value than that of cadmium complex. This principle is applicable to all complex ions. The overall stability constant of a complex is expressed by $\log\beta$ where β = sum of successive or stepwise equilibrium constant given by $\beta = \frac{[MLn]}{[M][L]^n}$. The factors governing the stability of a complex ion or species is obviously related to the metal M and Ligand L.

Metal factors are : (i) Charge and size (ii) Variation in d-orbitals (iii) Number of electrons in the d-orbitals (iv) Electronegativity of M. The ligand factors of stability are : (i) Electron donating capacity of the donor atom in the ligand, (ii) Basicity of the ligand, (iii) Chelate effect (iv) Ring size (v) Steric effect of the large ligands (vi) Entropy effect (vii) π-bonding effect of ligand.

Transition metals are particularly involved in complex formation. It is therefore essential to understand the electronic characteristics of the transition metals.

The Characteristics of the Transition Metals

The tendency of the elements to form complexes with various ligands or groups is very much dependent on the electronic structure of the particular atom. In most cases this appears to be a special characteristics of the transition elements. Although other non-transition elements also form complexes. The

remarkable characteristics of the transition metals to form complexes, in most cases coloured, having variable oxidation states and magnetic properties are mainly due to the presence of incomplete **d** orbitals. The intervening elements between group IIA and group IIIA in the Periodic Table are collectively referred to as Transition Elements. The transition elements may, therefore, be defined as those which have incomplete or partly filled **d** or **f** orbitals. Strictly speaking, the elements involving the incomplete **3d**, **4d** and **5d** orbitals are the transition elements and those involving incomplete **4f** orbitals are the inner transition elements or lanthanides or rare earths.

The transition elements in which **d** orbitals are generally being filled up with electrons are divided into three series. The first series involve **3d** orbitals from Sc (21) to Zn (30), the second series involve **4d** orbitals from Y (39) to Cd (48) and the third series involve **5d** orbitals from Hf (72) to Hg (80). Sometimes Zn, Cd and Hg are excluded from this group.

The filling up of **d** orbitals in transition metals is rather anomalous mainly on the consideration that the tendency is to attain stability by half-filled or completely filled **d** electron arrangements. The electronic configurations and the oxidation states of the first series of transition metals containing **3d** electrons are given in Table 24.1

Table 24.1. Electronic structures and oxidation states of the first series of the transition metals.

Metals	*At. No.*	*Electronic Structures*			*Oxidation states (+)*
Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6$	$3d^1$	$4s^2$	3,
Ti	22	"	$3d^2$	$4s^2$	2, 3, 4
V	23	"	$3d^3$	$4s^2$	2, 3, 4, 5
Cr	24	"	$3d^5$	$4s^1$	2, 3, 4, 5, 6
Mn	25	"	$3d^5$	$4s^2$	2, 3, 4, 5, 6, 7
Fe	26	"	$3d^6$	$4s^2$	2, 3, 4, 5,
Co	27	"	$3d^7$	$4s^2$	2, 3, 4
Ni	28	"	$3d^8$	$4s^2$	2, 3
Cu	29	"	$3d^{10}$	$4s^1$	1, 2
Zn	30	"	$3d^{10}$	$4s^2$	2

The formation of coloured ions and magnetic properties of transition metals are related to the presence of unpaired electrons in the system. A substance is called paramagnetic when it is attracted into a magnetic field. A diamagnetic substance is repelled by a magnetic field due to induced magnetism in the substance. Magnetic moments of substances are measured in terms of *Bohr magnetons* (BM). The values of Bohr magnetons indicate the number of unpaired electrons in a molecule of the substance and give informations regarding the structures. The relationship between the magnetic moment and unpaired electrons and also the colour of some transition metal ions in aqueous solutions are given in Table 24.2.

Table 24.2 Magnetic moments and colours of some transition metal ions as related to the number of unpaired electrons.

No. of unpaired electrons	*Magnetic Moment (BM)*	*Ionic species*	*Colour*
0	—	Ti^{+4}, Zn^{+2}	Colourless
1	1.7	Ti^{+3}	Purple
		V^{+4}, Cu^{+2}	Blue
2	2.8	V^{+3}, Ni^{+2}	Green
3	3.9	V^{+2}, Cr^{+3}	Violet
4	4.9	Cr^{+2}	Blue
		Mn^{+3}	Violet
5	5.9	Mn^{+2}	Rose

Colour is not only due to the presence of unpaired electrons but also due to other factors as well as electron transitions in presence of lights.

The d-orbitals play very important role in the formation of coordination compounds and the modern theories of the structures of inorganic complexes are based on the orientations of d-orbitals in space.

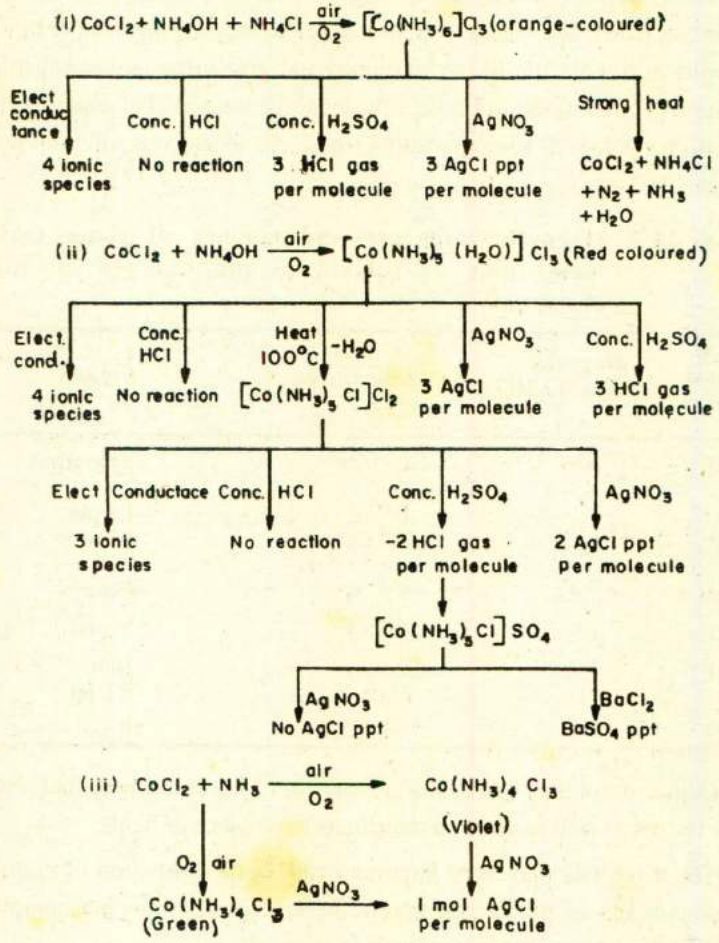
Synthesis and reactions of some Cobaltammine Complexes :

The orange-coloured $[Co(NH_3)_6]Cl_3$ is obtained by the reaction of aqueous pink $CoCl_2$ solution with NH_4OH and NH_4Cl by aerial oxidation.

(i) $CoCl_2 + NH_4OH + NH_4Cl \xrightarrow[O_2]{air} [Co(NH_3)_6]Cl_3$ (orange-coloured)

(ii) $CoCl_2 + NH_4OH \xrightarrow[O_2]{air} [Co(NH_3)_5(H_2O)]Cl_3$ (red coloured).

The reactions are shown in the following scheme :



The reactions indicate the stability of the complex compounds in course of the various chemical reactions. These complex compounds require the need of interpretation of their structures and mode of combinations.

Structures of the Complex Compounds

Complex compounds created a great difficulty regarding the nature of bonding present in such species. Many attempts were made in this direction but the most remarkable advancement for the interpretation of the structures of complexes according to the classical concept goes to the credit of Alfred Werner. He advanced a brilliant theory to explain the characteristics of complex compounds and also predicted future developments in the field of structural chemistry. For his pioneer contributions Werner was awarded the Nobel Prize in chemistry in 1913.

Werner's Theory : The theory is known as the Coordination Theory of Complex Compounds and is based upon certain assumptions using the classical concept of valency which are summarized below :—

1. Metals possess two types of valencies :

   (a) Primary valency and (b) Secondary valency.

2. Primary valency combines the acidic and basic radicals or ions and hence the components united by this valency are ionizable. Simple covalent compounds are also formed by primary valency. Thus NaCl, CCl_4, NH_3, $FeCl_3$ are compounds formed by primary valency. These are both ionic and covalent compounds.

3. Secondary valency combines simple molecules or groups which are capable of independent existence, as well as the negative radicals to the metal atoms or ions. The components united by this valency are not capable of ionization. Thus $AgCl.2NH_3$; $CuSO_4.5H_2O$; $K_4[Fe(CN)_6]$ etc.

4. Every complex compound has a metal atom situated at the *centre* of a co-ordination sphere. The neutral molecules or ions united to the central atom by secondary valency are within the coordination sphere. The number of groups or ions so combined to the central atom is called the coordination number of the central metal atom.

Thus in $[Cu(NH_3)_4]SO_4$ copper is the central metal atom. $4NH_3$ are united to Cu by secondary valency and exist within the coordination sphere and 4 is the coordination number of copper. The attached groups or molecules are called co-ordinated groups or Ligands. SO_4^{-2} ion is combined to copper by means of primary valency and neutralizes the +2 charge of Cu.

5. The fulfillment of coordination number appears to be an essential criterion in complex compound formation.

6. The secondary valencies are directed in space about the central metal ion. The coordinated groups are arranged in symmetrical manner at the corners of geometrical figures in space. Thus, 6 groups are situated at the corners of a regular octahedron, shown in Fig. 24—1.

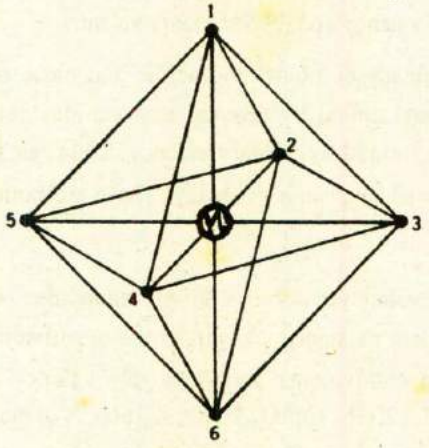


Fig. 24—1. Octahedral configuration. M is the central metal atom.

Werner's Theory predicts the existence of isomerism which has been experimentally proved. The examples of the structures of some complex compounds according to Werner's theory are illustrated in Fig. 24—2.

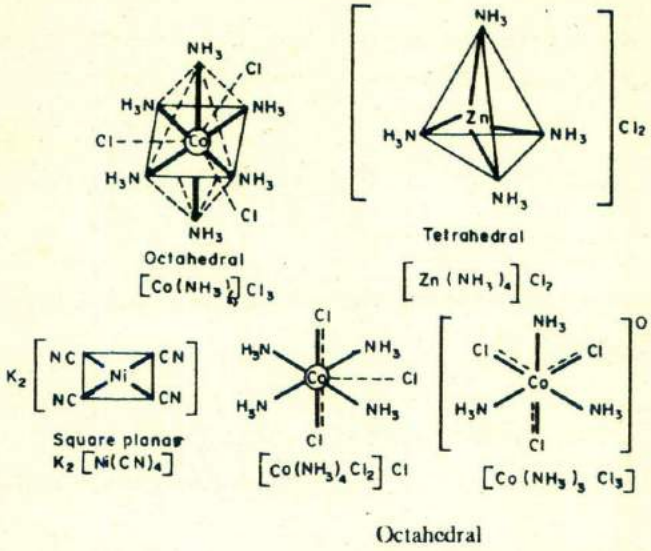


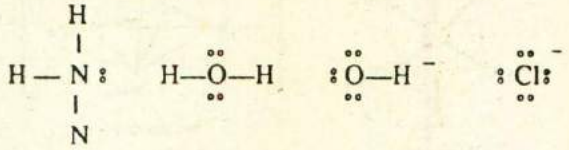
Fig. 24—2. The structure of complex compounds, $[Co(NH_3)_6]Cl_3$, $K_2[Ni(CN)_4]$, $Zn(NH_3)_4Cl_2$, $[Co(NH_3)_4Cl_2]Cl$ and $[Co(NH_3)_3Cl_3]$ according to Werner.

Werner's theory had some serious drawbacks. No theoretical reasons for assuming the two types of valency and the space configurations of the co-ordinated groups were given. Formulations of complexes, such as $K_4[Fe(CN)_6]$, $Na_3[Co(NO_2)_6]$ are not satisfactory. No explanation as regards the particular coordination number of metal was given.

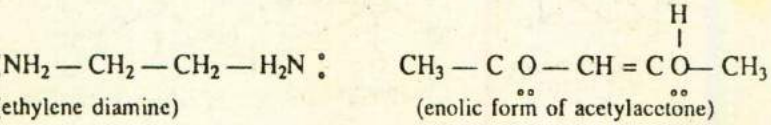
Electronic Interpretation of the Structure of Complex Compounds

Sidgwick's Theory : An electronic theory of the structure of complex compounds was put forward by Sidgwick in 1923. According to this theory the formation of a complex compound involves the donation of an electron pair by each coordinating group or ligand to the metal atom. Each coordinating group has at least one lone pair of electrons which are used for the formation of co-ordination bonds with the metal atom by sharing. In the formation of NH_4^+ ion a proton accepts and shares the lone pair of electrons from the nitrogen of NH_3 (Lewis acid-base reaction) :

Thus NH_3 has one lone pair, H_2O has two lone pairs OH^- has three lone pairs and Cl^- has four lone pairs.

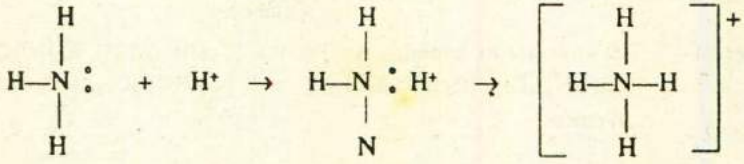


Some groups or ions have two or more than two atoms with lone pair for donation to metal atoms.

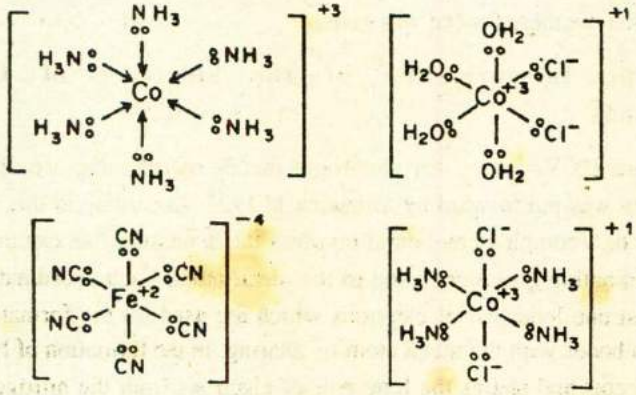


(ethylene diamine)

(enolic form of acetylacetone)



Similarly, a metal ion coordinates with a number of groups or ions containing at least one lone pair electrons. Thus $6NH_3$ or $6H_2O$ become coordinated to Co^{+3} ion and $6CN^-$ coordinated to Fe^{+2} ion to give complex ions :



In the above examples, it is seen that the net charge of the complex ion is the algebraic sum of the oxidation number of the central atom and the oxidation numbers of the coordinating group. The question as to why the metal ion coordinates with a large number of groups or ions by means of coordination bonds was explained from the point of view of the effective atomic number of the metal atoms.

Some groups may have possibilities of coordinating with metals by donation from any site as in

$$CO \quad \left(:C \equiv O:\right), \qquad CN^- \quad \left(:C \equiv N:\right)^-,$$

$$NO_2 \quad \left(: \overset{\overset{O}{\uparrow}}{N} \equiv O:\right) \text{ or } \left(:O - N = O:\right)$$

Effective Atomic Number (E. A. N.)

The effective atomic number of a metal atom in a complex is obtained by subtracting from the atomic number of the metal, the number of electrons lost in ion formation and adding the total number of electrons gained in coordination (two electrons from each coordinating group). Thus,

$$E.\ A.\ N. = A - El + Eg$$

where A is the atomic number of the metal atom;
El, number of electrons lost in ion formation ;
Eg, Total number of electrons gained in coordination, each ligand donating two electrons.

Sidgwick pointed out that the formation of the complex compounds is caused by a *tendency of the central metal atom to attain the electronic configuration of an inert gas.* That is the effective atomic number of the metal atom after complex formation becomes equal to the atomic number of an inert gas.

Thus in $K_4[Fe(CN)_6]$ the atomic number of Fe is 26 and number of electrons lost to form Fe^{+2} ion is 2. The 6 coordinated groups donate a total of $2 \times 6 = 12$ electrons which are gained by Fe^{+2} ion in coordination. Thus E.A.N.

of Fe in $K_4[Fe(CN)_6]$ is 26 −2 + 12 = 36 which is the atomic number of krypton. This was considered to be the reason for the stability of $[Fe(CN)_6]^{-4}$ ion. The effective atomic number of some of the metal atoms forming complex compounds are given in Table 24·3.

Table 24.3. The effective atomic number of some metal ions in complexes.

Metal ions	*Atomic number*	*Coordination number*	*Electrons lost in ion formation*	*Electrons gained in coordination*	*E.A.N.*
Fe^{+2}	26	6	2	12	36(Kr)
Co^{+3}	27	6	3	12	36(Kr)
Zn^{+2}	30	4	2	8	36(Kr)
Pd^{+4}	46	6	4	12	54(Xe)
Pt^{+4}	78	6	4	12	86(Rn)
Hg^{+2}	80	4	2	8	86 (Rn)

In a nutshell Sidqwick's theory of coordination compounds may be summarised in the following points :

1. Groups coordinating with metal atom or ions contain lone pairs of electrons.
2. The lone pairs are donated to the metal atom or ions forming coordination bonds.
3. The number of groups or ligands are coordinated to the metal atom or ions according to Effective Atomic Number rule.
4. Effective Atomic Number of the metal atom or ion corresponds to that of an inert gas thereby imparting stability to the complex compounds.

Limitations of Sidgwick's Theory : (1) There are quite a large number of complex ions in which the effective atomic numbers of metal atoms are not those of the inert gases. It may have either less or more electrons than an inert gas. Yet the complexes formed are quite stable. This point is illustrated by some examples in Table 24.4.

Table 24.4. E.A.N. of metal atoms of some complexes (Non-inert gas).

Metal ions	*Atomic number*	*Coordination number*	*Electrons lost in ion formation*	*Electrons gained in coordination*	*E.A.N.*
Cr^{+3}	24	6	3	12	33
Fe^{+3}	26	6	3	12	35
Ni^{+2}	28	6	2	12	38
Pd^{+2}	46	4	2	8	52
Ag^{+}	47	2	1	4	50

(2) Sidgwick attempted to explain this drawback in the electronic theory on the basis that the tendency of the metal atom is not only to attain the inert gas configurations but also to produce symmetrical structures (planar, tetrahedral, octahedral etc.), irrespective of the actual numbers of electrons involved. But the bonding character of the lone pair of electrons from the ligands to the metal could not be satisfactorily explained since the lone pair electrons ordinarily have opposed spins (anti-bonding property).

(3) The theory does not explain the geometry of the molecules.

(4) Metals with odd atomic numbers in many cases do not obey the E. A. N rule

(5) Magnetic properties of some complexes and isomerism could not be explained.

The electronic theory of complex compounds has been developed to a very great extent and is one of the most advanced field of chemistry. Salient points from the modern theories are given.

Pauling's Theory (Valence Bond Theory)

According to the Valence Bond Theory the donation of an electron pair by each coordinating group for the creation of coordination bonds involves the orbitals of the central metal atom into which the donated electrons enter. The important features of Valence Bond Theory (VBT) are : –

(1) The electron pairs of the groups acquire bonding characteristics because of hybridization, such as sp^3 in NH_3, PH_3, H_2O etc. and may also be pure p or s orbital electrons as in the cases of Cl^-, F^- and H^- ions etc.

(2) The electron pairs from the coordinating groups enter into the vacant, vacated and available orbitals of the metal atom with or without rearrangements of electrons present in the metal orbitals.

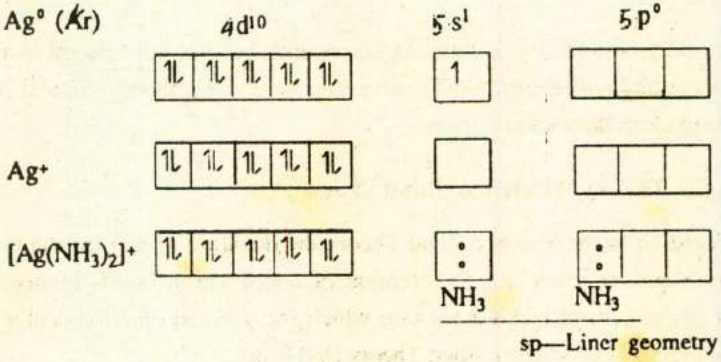
(3) The electrons from the coordinating groups enter into the vacated, vacant and available orbitals of the metal, two electrons in each, forming hybrid orbitals directed in space. The electronic arrangements determine which of the possible geometrical structures the complex will assume. Thus,

sp—linear	sp^3—tetrahedral	dsp^2—square planar
sp^2 — trigonal		dsp^3 — trigonal bipyramidal
		dsp^3 — square pyramidal

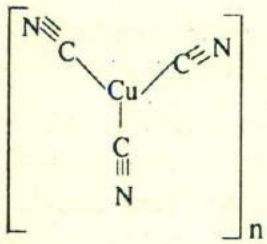
d^2sp^3 or sp^3d^2—octahedral.

The formation of hybrid bonds in some complex compounds are illustrated to show space arrangement of the coordinated groups about the central metal atom through the concept of hybridization of orbitals according to VBT.

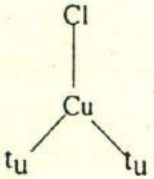
1. Coordination Number (C. N.) = 2 : Only a few complexes have C. N. = 2. These are $[N \equiv C—Ag—C \equiv N]^-$, $[Cl\text{-}Au\text{-}Cl]^-$, $[H_3N\text{-}Ag\text{-}NH_3]^+$, $[Cl—Cu^+—Cl]^-$ etc. The metals use sp hybrid orbitals and the complexes have linear geometry.



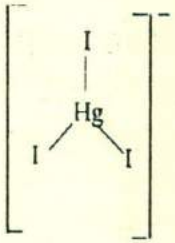
2. Coordination Number (C. N.) =3 : Complexes having C. N. = 3 are uncommon. Some examples are given. These have metals using sp^2 hybrids $[Cu^+ Cl(tu)_2]^\circ$, $[Cu(CN)_2]^-$, $KHgI_3$ $Cu[S_3(PR_3)_3]$ etc.



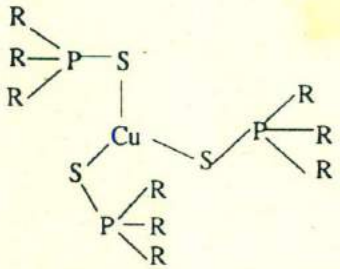
$[Cu(CN)_2]_n$ Polymer



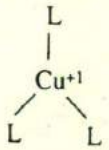
bis (thiourea) Cu(I)

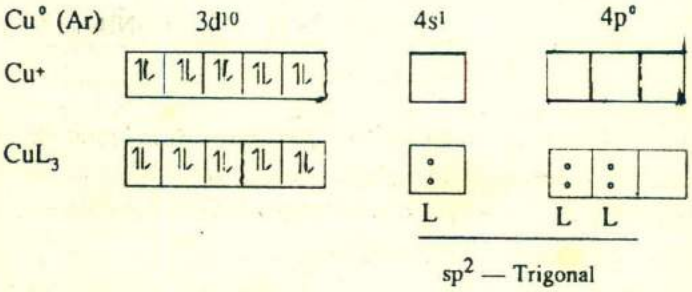


$KHgI_3$



Tris (trimethyl phosphine sulphide) Cu (I)





3. Coordination Number (C. N.) = 4 : The Complexes having C. N.=4 may assume two types of geometries: (i) Tetrahedral (ii) Square Planar.

Tetrahedral Complexes :

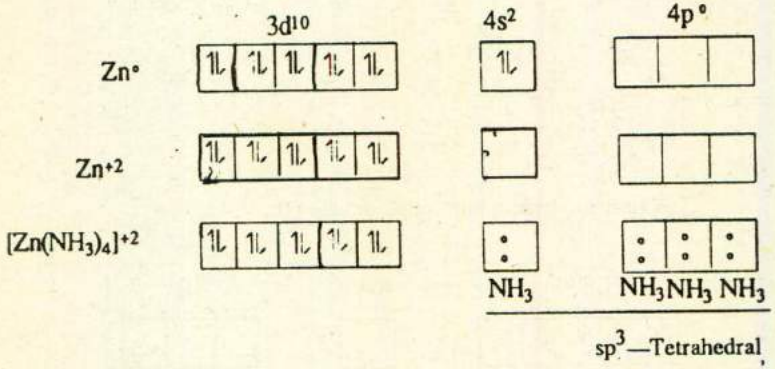
Tetrahedral complexes are most numerous such as :

$[BH_4]^-$, $[AlH_4]^-$, $[BeF_4]^{-2}$, $[Zn(NH_3)_4]^{+2}$, $[Cd(CN)_4]^{-2}$

$[Ni(CO)_4]^0$ and also MnO_4^-, CrO_4^{-2} etc are some examples of tetrahedral structures. They have metals using sp^3 hybrid orbitals for complex formation.

$[Zn(NH_3)_4]^{+2}$: When the orbitals of Zn^{+2} ion coordinate with four NH_3 molecules to form the complex ion $[Zn(NH_3)_4]^{+2}$, each nitrogen atom of NH_3 molecules donates its lone pair of electrons to Zn^{+2}. These donated electrons occupy the vacant 4s and 4p orbitals of Zn^{+2} ion as shown below. The vacant orbitals are shown by empty boxes.

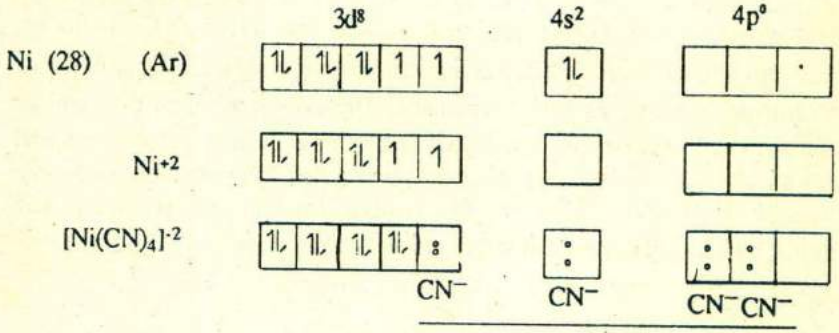
$Zn(30)—1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3s^{10}\ 4s^2$

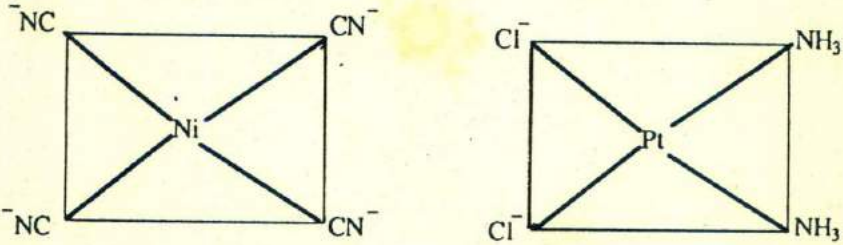


Thus a pair of electrons from each NH_3 goes to one 4s and three 4p vacant orbitals combined as $4s4p^3$ hybrid orbitals or simply sp^3 hybrid orbitals. Thus the four NH_3 molecules are arranged at the corners of a tetrahedron with Zn^{+2} which has its 4 coordination number satisfied.

Common tetrahedral compounds include $[Zn(CN)_4]^{-2}$, $[Cd(CN)_4]^{-2}$, $[Hg(CN)_4]^{-2}$, $[Cu(CN)_4]^{-3}$, $[BeF_4]^{-2}$, $Ni(CO)_4$, $[CuCl_4]^{-2}$ and even anions such as MnO_4^-, CrO_4^{-2} etc.

Square planar geometry :





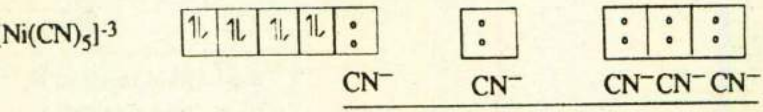
Square plar geometries of $[Ni(CN)_4]^{-2}$ and $[Pt(NH_3)_2Cl_2]$

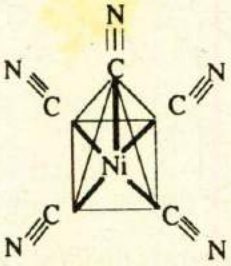
Square planar Complexes :

Square planar are not very common because of sterical factors. Some metal ions form square planar complexes particularly those having d^8 ions such as Ni^{+2}, Pd^{+2}, Pt^{+2} and Au^{+3}. Co^{+2} (d^7) may form square planar compounds. In the cases of chlorophyll and other biocomplexes the square planar forms of the metal complexes are forced by the rigid structures of large ligands such as porphyrine groups etc.

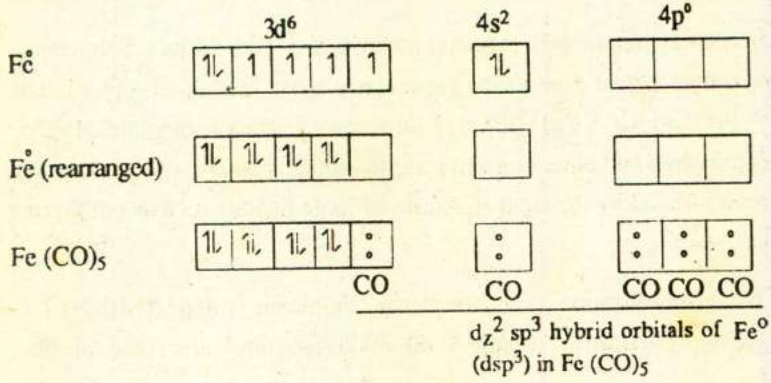
The bond hybridization in square planar complexes is **dsp^2**. $[Ni(CN)_4]^{-2}$, $[Pt(NH_3)_2Cl_2]$, $[NiDmg_2]^{o}$, (Dmg = dimethylglyoxime) are some of the examples.

4. Coordination number (C. N.) = 5 : 5-coordinated complexes are much less common as compared to C. N. 4 or 6. Complexes apparently considered to have C. N. = 5 such as Cs_3CoCl_5 and $(NH_4)_3ZnCl_5$ actually contain discrete tetrahedral MCl_4^{-2} anions and free chloride ions. Recently some 5-coordinated complexes have been made. These have trigonal bipyramidal geometry which may be regular and distorted forms as well as square pyramidal forms having both regular and distorted geometries. Thus pentachlorocuprate (II) anion in $[Cr(NH_3)_6][CuCl_5]$ has regular bipyramidal geometry and $[Cr(en)_3]$ $[Ni(CN)_5]$ has distorted square planar configuration.

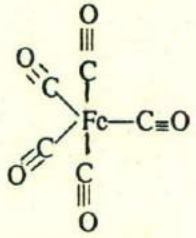




dsp^3 i.e. **($d_{x^2-y^2}$) sp^3** hybrid orbitals of Ni leads to square pyramidal geometry of $[NiCl_5]^{-3}$ ion. $Fe(CO)_5$ has regular trigonal bipyramidal geometry



involving **dsp³** ($d_{z^2}sp^3$) hybrid orbital of Fe° give trigonal bipyramidal geometry



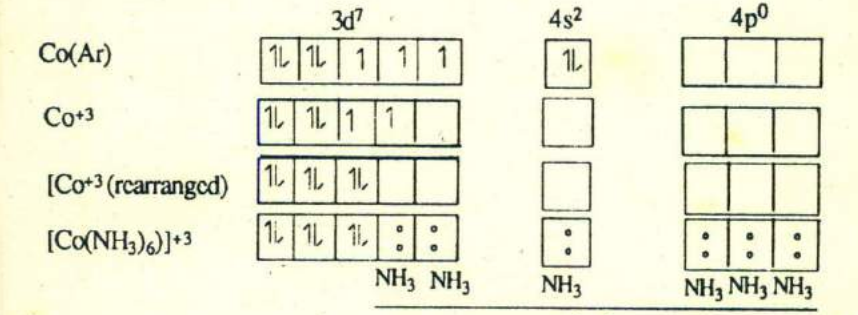
Trigonal bipyramidal geometry of $Fe(CO)_5$

5. Coordination Number (C. N.) = 6 :

Of all the coordination complexes known, those containing 6-coordinated bonds having octahedral geometry are most numerous. Transition metals as well as non-transition elements form large number of species. Examples like $[Al(H_2O)_6]^{+3}$, $[Ti(H_2O)_6]^{+3}$, $[Pt(Cl)_6]^{-2}$, $[Fe(CN)_6]^{-3}$ and the most discussed case of $[Co(NH_3)_6]^{+3}$ are familiar. Examples.

$[Co(NH_3)_6]^{+3}$ complex ion :

Co (27) — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$

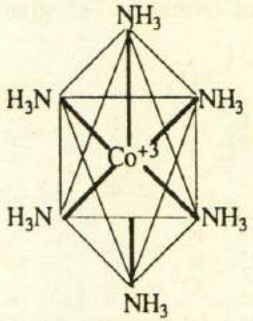


d^2sp^3 hybrid orbitals of Co^{+3}

d^2sp^3 is actually **$(dx^2\text{-}y^2\ dz^2)sp^3$** hybrid orbitals giving octahedral geometry.

Thus 12 electrons from $6NH_3$ molecules enter into two **3d**, one **4s** and three **4p** orbitals, two electrons from each. Since all the 6 bonds in the $[Co(NH_3)_6]^{+3}$ complex ions are completely equivalent, the formation of six **d^2sp^3** hybrid bonds take place which are directed in space with octahedral geometry.

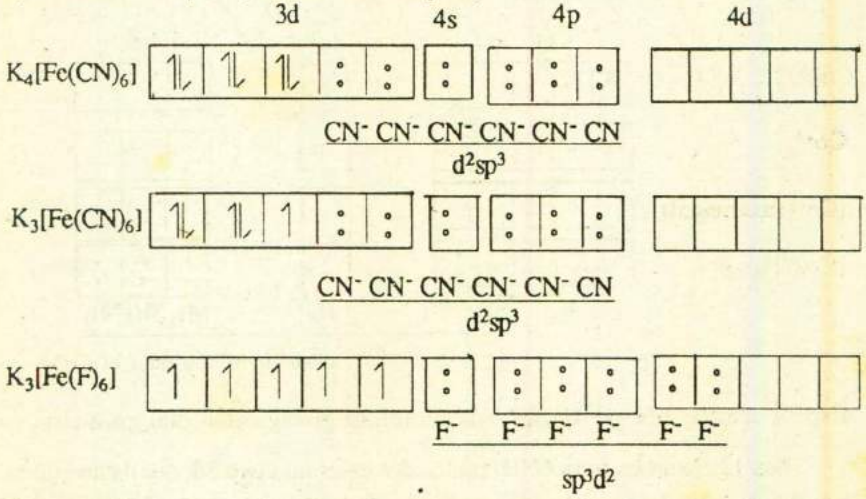
d^2sp^3 ($d_{x^2-y^2}$, d_{z^2}) sp^3 hybrid orbitals having octahedral geometry :



Octahedral geometry of $[Co(NH_3)_6]^{+3}$ ion

The oxidation of Co^{+2} in presence of some ligands has been considered as an achievement of VBT. Thus $[Co(H_2O)_6]Cl_2$ in presence of NH_3 as ligands oxidizes Co^{+2} to Co^{+3} forming $[Co(NH_3)_6]^{+3}$.

$K_3[Fe(CN)_6]^{-3}$ like $[Co(NH_3)_6]^{+3}$ has the octahedral geometry since Fe^{+3} uses d^2sp^3 hybrid orbitals but has one unpaired electron in the **d**-orbital thereby acquiring the magnetic property. However, $[Fe(F)_6]^{-3}$ although has the same octahedral geometry but possesses five unpaired electrons. In the latter case the hybridization is sp^3d^2 (outer orbital complex).



The most important noticeable effect of the rearrangement of electrons during complex formation is the appearance of paired and unpaired electrons.

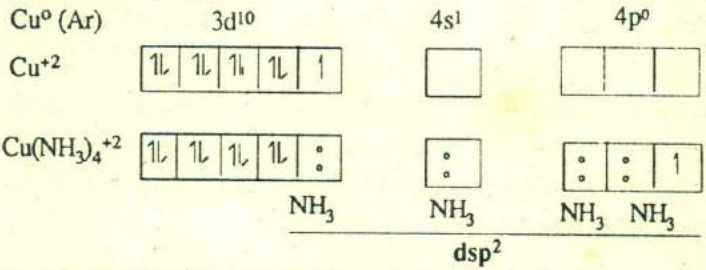
This manifests itself in the magnetic properties of the compounds before and after complex formation. Compounds with unpaired electrons are attracted into magnetic fields and are called paramagnetic. Thus $K_3Fe(CN)_6$ and K_3FeF_6 are paramagnetic complexes having 1 and 5 unpaired electrons respectively. Compounds containing paired-up electrons are not attracted into the magnetic field but tend to move out. Such substances are called diamagnetic. $[Co(NH_3)_6]Cl_3$ and $K_4[Fe(CN_6]$ are diamagnetic complexes.

The Limitations of Valance Bond Theory.

(a) The valence bond theory does not explain many of the physical properties of the complex compounds, such as absorption spectra, heats of formation, heat of hydration, stability constant etc.

(b) The peculiar behaviour of divalent metal ions (d^8 ions), such as Ni^{+2}, Pd^{+2}, Pt^{+2} which form dsp^2 hybrid bonds to give square planar complexes instead of the expected 5-coordinated dsp^3 bonds, is not explained.

(c) The major weakness of valence bond theory is the bonding in Cu^{+2} complexes which is supposed to use dsp^2 hybrid orbitals. Cu^{+2} is a d^9 ion and a complex of Cu^{+2}, such as $[Cu(NH_3)_4]^{+2}$ has square planar structure according to valence bond theory. Thus,



In order that dsp^2 bonds are formed, the unpaired electron in 3d must be promoted to a high energy level, such as in 4p as shown above. This gives instability to the complex and the unpaired electron should be easily lost producing a Cu^{+3} state. But this does not happen. Cu^{+2} complexes are stable compounds.

(d) The magnetic moments of some complexes of the same transition metal are widely different. Thus the Fe^{+3} complexes. $K_3Fe(CN)_6$ and $K_3Fe(F)_6$ have magnetic moments 1'7 and 6'0 B.M. (Bohr Magneton) corresponding to one unpaired electron and five unpaired electrons in their respective molecular structure.

(e) The distortions in molecular structures have not been explained.

These and other limitations have been successfully explained from the point of view of the Crystal Field Theory (CFT) or Ligand Field Theory (LFT) which provides a simple explanations regarding the structures o. complexes.

The structures of complexes have also been explained on the basis of valence shell electron pair repulsions as discussed in Chapter 5 mainly for compounds of non-transition elements but the presence of d electrons produce a great deal of deviations as expected.

Isomerism in Complex Compounds

Since the groups coordinated to metal atoms in complexes are situated in space, there can be various modes of their arrangements. This situation gives rise to the phenomenon of isomerism in complex compounds. Isomers are defined as compounds having the same formula but different structures. Again, because of the different types of bonding system and the various ways of arranging the co-ordinated groups, a large number of different types of isomerism are exhibited by the inorganic complex compounds. Some of these types of isomerism are discussed.:

1. Ionization isomerism, 2. Hydrate isomerism, 3. Linkage isomerism, 4. Geometrical isomerism, 5. Optical isomerism, 6. Polymerisation isomerism. 7. Coordination isomerism 8. Ligand isomerism 9. Ring size isomerism. 10. Electronic isomerism etc.

A brief description of some important types of isomerism is given with reference to the 6-coordination complexes (complexes containing 6-coordinated groups).

1. Ionization isomerism : Complexes containing the same chemical composition but giving different ions in solution are called ionization isomers. Thus $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ are ionization isomers. In solution these compounds give tests of SO_4^{-2} and Br^{-1} ions respectively. Similarly, $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$ are differently ionized in solution. The acidic groups within the coordination sphere are not ionizable.

2. Hydrate isomerism: Water molecules coordinate with metal ions through the electron pair of oxygen. It can also combine with a complex as water of crystallisation. Isomerism exhibited by complex compounds due to the different mode of combination of water molecules is called hydrate isomerism. Thus $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2.H_2O$ are hydrate isomers.

Similarly, $[Co(NH_3)_4H_2O.Cl]Br_2$ and $[Co(NH_3)_4\ Br_2]Cl.H_2O$ are hydrate isomers.

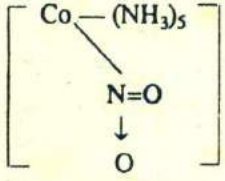
These hydrate isomers show difference in physical and chemical properties and also in colour.

3. Linkage isomerism : Linkage isomerism or structural isomerism occurs when a coordinated group has two or more atoms which can function as electron donor. Thus in the nitro group, NO_2^- the donor atom may be either N or O. Similarly, in the thiocyanate group, SCN^-, the donor atom may be S or N. Isomerism exhibited by complexes due to different modes of coordination of the same group with metal ion is known as linkage or structural isomerism. This arises due to the electronic arrangement in the molecular structures of the coordinated group. Thus NO_2^- group has structures (I) and (II) :

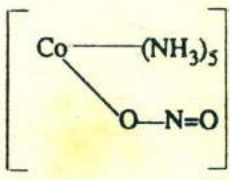
$$\underset{\downarrow}{\overset{}{-N=O}} \qquad\qquad -O-N=O$$
$$O \quad (I) \qquad\qquad (II)$$

$\overset{\cdot\cdot}{S}—C \equiv N$ and $\overset{\cdot\cdot}{N} \equiv C—S$ also produce linkage isomerism.

The cobalt complex, therefore, has two forms :



Cl_2 or



Cl_2

4. Coordination isomerism : Complexes containing both cations and anions as coordinated compounds exhibit coordination isomerism.

$[Co(NH_3)_6]\ [Cr(SCN)_6]$ and $[Co(SCN)_6]\ [Cr(NH_3)_6]$,

$[Cr(NH_3)_4(CN)_2][Co(NH_3)_2(CN)_4]$ and $[Co(CN)_2(NH_3)_4][Co(CN)_4(NH_3)_2]$ are isomers

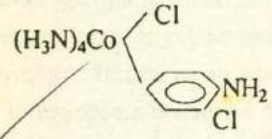
5. Polymerisation isomerism : The units of the polymers are of different complexity. Thus in $[Co(NH_3)_3(NO_2)_3]_n$, 9 isomers occur. Similarly $[Co(OH)_3\ CoX_3.\ 6NH_3]_2$ units are present in the following complexes which exhibit polymerisation isomerism.

$[(H_3N)_3Co(OH)_3\ Co(NH_3)_3]_2\ X_6$ and

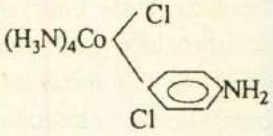
$[Co\{(OH)_2\ Co(NH_3)_4\}_3]X_6$

6. Ligand isomerism : Ligands having different structures and different chemical species produce ligand isomerism.

$[H_3N)_4CoSO_3SCN]$ and $[(H_3N)_4\ CoS_2O_3CN]$ and also the following are ligand isomers :



and



7. Electronic isomerism : Isomerism arises due to different electron distributions between metal and ligands.

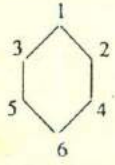
$[(H_3N)_5CoNO]^{+2}$ and $[(H_3N)_5\ CoNO]^{+3}$

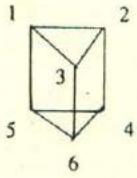
These may have Co^{+2}, Co^{+3}, NO, NO^- and NO^+ species in the molecular structures.

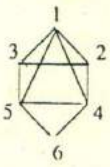
8 Geometrical isomerism : This is also known as stereoisomerism or cis-trans isomerism . This is the most important type of isomerism in the co-ordination compounds and is a direct outcome of the arrangement of the co-ordinated groups in space. The geometrical isomerisom is based on the geometry of the coordination complexes and is exhibited by compounds of 6-coordination numbers and also by other coordination numbers.

It may be noted that when the coordinated groups are the same, no geometrical isomerism is possible. Geometrical isomerisom is possible only when there are at least two groups different from the rest as in (MA_4B_2) in the octahedral and (MA_2B_2) in square planar complexes, where M is the metal atom and A and B are the different groups.

In fact the two isomers in MA_4B_2 was the convincing proof of the octahedral geometry since other hexa-coordinated or substituted forms of MA_4B_2 have different configurations



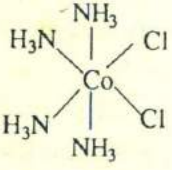




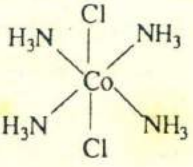
Experimental

	plane hexagon	trigonal prism	octahedron	
MA_5B	1 Isomer	1 isomer	1 isomer	1 isomer
MA_4B_2	3 Isomers	3 isomers	2 isomers.	2 isomers.
MA_3B_3	3 isomers	3 isomers	2 isomers	2 isomers

For example, $[Co(NH_3)_4Cl_2]Cl$ will have two isomers due to different arrangement of the 2Cl within the complex ion; the ionic Cl^- is not shown in the diagrams below :

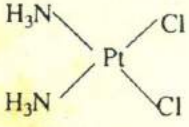


Cis-isomer

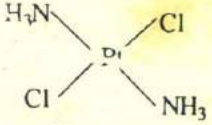


Trans-isomer

The two Cl may be adjacent to each other or may be apart. When the positions of the coordinated group are adjacent to each other the complex is known as a *cis-complex*. When the groups are situated diagonally opposite to each other the compound is known as a *trans-complex*. Similar is the case with $[Pt(NH_3)_2Cl_2]$, a 4-coordination complex :

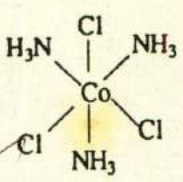


Cis-isomer

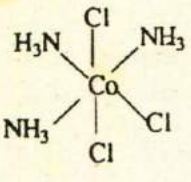


Trans-isomer

Geometrical isomerism or cis-trans isomerism is also exhibited by compound MA_3B_3 type as in $[Co(NH_3)_3Cl_3]$.



Cis, cis, cis



Cis, cis, trans

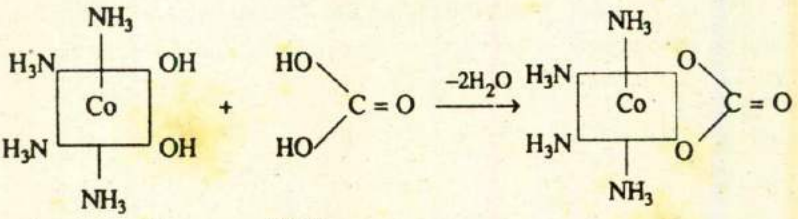
9. Optical isomerism : This is also known as mirror-image isomerism. In most cases when chelates (groups or ligands or species such as $NH_2—CH_2—CH_2—NH_2$ form two N—M bonds) enter into 6-coordinated complexes forming compounds of the type $Co(en)_2AB$ where (en) stands for $NH_2CH_2CH_2NH_2$ and A and B are the different groups coordinated to cobalt, both cis-and trans-forms are possible. The cis forms show optical isomerism. (See page 707)

Determination of Cis-Trans isomers :

Both instrumental and chemical methods are applied for the identification of cis-trans configurations of the coordination complexes. Instrumental methods consist of spectral studies, x-ray diffraction, dipole moment etc. The chemical methods are based on reactions. These are :

(i) Introduction of a bifunctional group : A bifunctional group is also known as *bidentate* group. The process of introducing a bifunctional group in a complex structure is known as *chelation.* A bifunctional group "bites" the metal ion at two positions. These groups are :

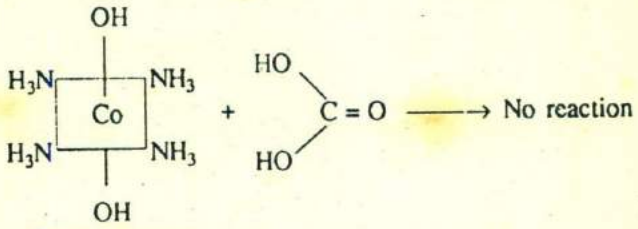
$NH_2—CH_2—CH_2—NH_2$, NH_2CH_2COOH, CO_3^{-2}, $C_2O_4^{-2}$ etc.



Cis-compound

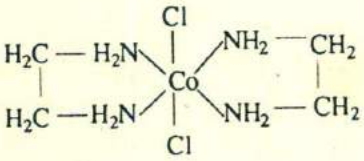
H_2CO_3
CO_3^{-2} (bifunctional group)

Reaction occurs

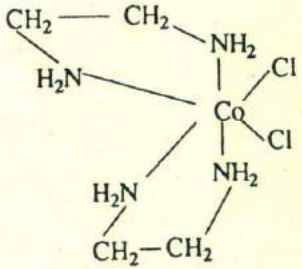


Trans-compound

A more common group is ethylenediamine $NH_2CH_2CH_2H_2N$ (en) in which the two N atoms coordinate in two, four or all the 6 positions of 6-coordinated complexes i.e. one (en), two (en) or three (en). Cis-trans isomers identified through coordination of two (en) quite clearly.

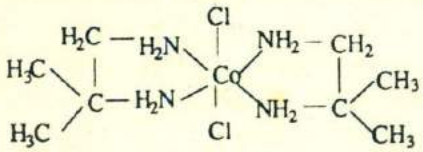


Trans isomer

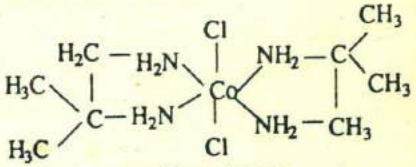


Cis isomer

Substituting another group in the organic part of trans isomer also gives cis-trans isomer. This is also an example of Ligand isomerism.



Cis-isomer



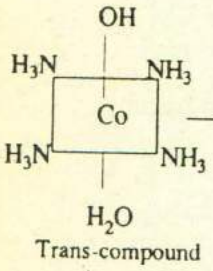
Trans-isomer

(ii) *Diol formation*

Consider the reaction :

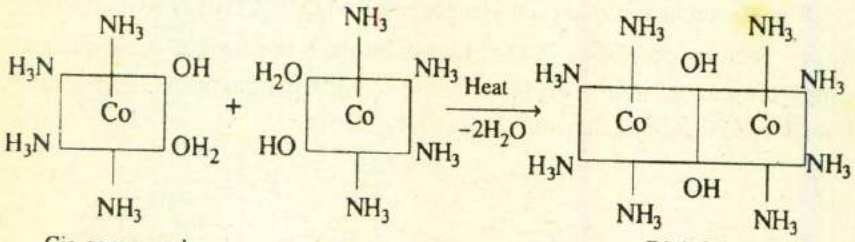
$$[Co(NH_3)_5\,H_2O]\,Cl_3 \xrightarrow{heat} [Co(NH_3)_5Cl]Cl_2$$

No diol formation



Heat ⟶ No diol formation since OH and H_2O are in trans positions.

Trans-compound



Cis-compound Diol formation

Simply the reaction may be represented as :

$$[Co(NH_3)_4(H_2O)OH]^{+2} + [Co(NH_3)_4(H_2O)OH]^{+2} \xrightarrow{-2H_2O}$$

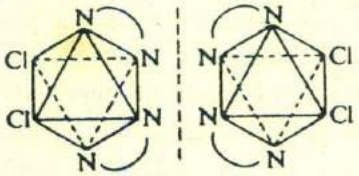
$[(H_3N)_4Co(OH)_2Co(NH_3)_4]^{+4}$ which is a diol (*polynuclear complex*)

Only the cis-compounds with appropriate ligands formed the dinuclear (containing two metal atoms) or a diol (complexes containing two OH groups). OH group acts as a bridge group between the two Co atoms. Other bridge groups are : —NH—, —SH—, —O— etc. and may combine two or more metal complexes forming polynuclear species with one, two or three bridge groups.

Optical Activity in complexes :

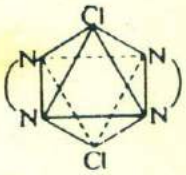
(iii) Obviously, the trans-form is symmetrical and, therefore, has a plane of symmetry. But the cis-form has a mirror-image which is not superimposable and thus does not possess any plane of symmetry. Such molecular structures are found to be optically active, i. e., they rotate the plane of a polarized light. A large number of inorganic optically active complex compounds have been found to exist. The cis-form $[Co(en)_2NH_3Cl]Br_2$ has been found to be optically active because the mirror-image form is not superimposable :

$NH_2\,CH_2\,CH_2\,H_2N$ represented as N⌒N or en



cis

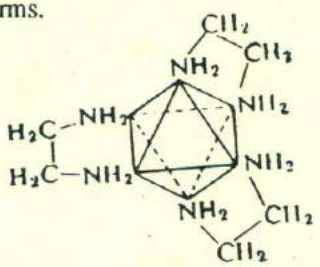
Cis-forms are optically active (Non-symmetrical)

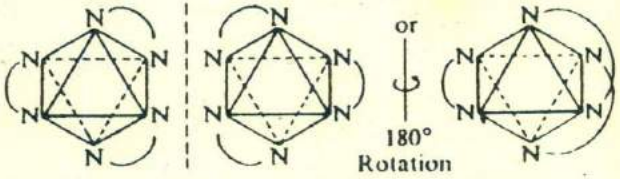


trans

trans-form not optically active (symmetical)

Optical activity is retained even when A=B (both are NH_3 or Cl). Compounds of the compositions $[Co(en)_3]^{+3}$ are also optically active and are enantiomorphs. Some need resolutions into *d*- and *l*-forms.





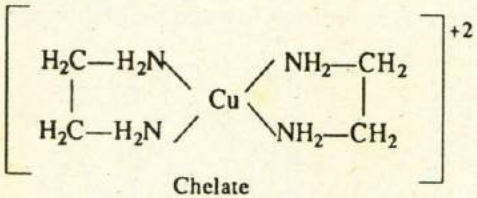
Optical isomers (en = $NH_2\,CH_2\,CH_2\,NH_2$)

Chelate complexes : In the following examples the coordinated group has only one atom which donates a pair of electrons to form a coordinated bond with the central metal ion and, each group occupies only one position :

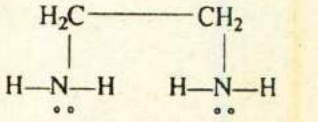
$[Cr(H_2O)_6]^{+3}$ $[Co(NH_3)_6]^{+3}$ $[Ag(NH_3)_2]^{+}$ $[Ni(CN)_4]^{-2}$

Such groups or ligands are called *monodentate* ligands. But there are groups which may have two or more atoms which coordinate with the metal atom simultaneously and occupy two or more positions in the molecular structure. The ligands are known as bidentate, tridentate or polydentate.

A coordinating group or ligand that occupies two or more coordination positions in a complex and contributes more than a single pair of electrons is known as a *chelate group*, and the complex is known as *Chelate*. The process by which chelates are formed is called *Chelation*. Thus $C_2O_4^{-2}$ ion, ethylenediamine, $NH_2CH_2CH_2NH_2$, glycine, etc donate electrons to the metal atom at the same time occupy two positions in the complexes. Thus $NH_2CH_2CH_2NH_2$ has two nitrogen atoms and each has a pair of electrons for coordination with, say, Cu^{+2} ion. Hence only two molecules of $NH_2CH_2CH_2NH_2$ will satisfy the coordination number 4 of Cu^{+2} ion forming $[Cu(NH_2—CH_2—CH_2—NH_2)_2]^{+2}$ having the following configuration in the molecular structure :

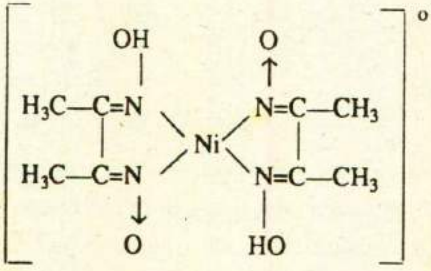


Chelate
Cu—ethylenediamine



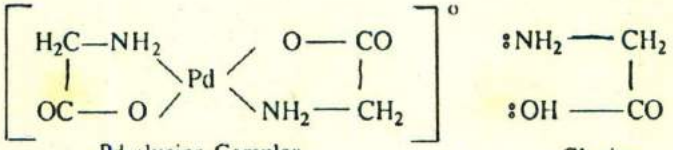
Chelate group
(ethylenediamine)

Dimethyl glyoxime which is generally used for identification and quantitative determination of nickel also occupies two positions in the complex having the structure :



Ni—dimethyl glyoxime Complex

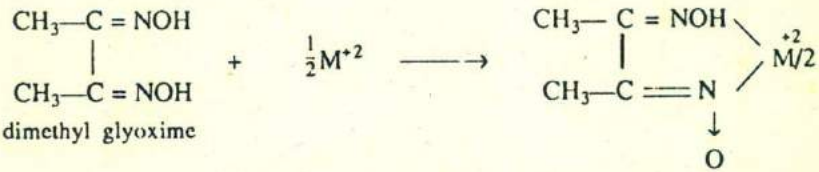
Similarly, NH_2CH_2COOH also provides two atoms for the formation of chelate. Thus with Pd^{+2} :



Pd-glycine Complex Glycine

Notice that there is difference between the charges of the complex ions formed by ethylenediamine, dimethyl glyoxime and glycine. Ethylenediamine has two nitrogen atoms which provides the two pairs of electrons to Cu^{+2} ion and, therefore, satisfies the coordination member 4 of Cu^{+2} ion by two molecules of $NH_2CH_2CH_2NH_2$ The dimethyl glyoxime and glycine not only satisfy the coordination number but also neutralize the charges on the metal ion, that is, satisfy the oxidation number of the metal ion at the same time, because the molecules of dimethyl glyoxime and glycine have H atoms which can be replaced by metals. It means that the acidic part of these groups also acts simultaneously. These produce electrically neutral complexes. The lone pairs of electrons on O in OH provide the coordinating electrons :





dimethyl glyoxime

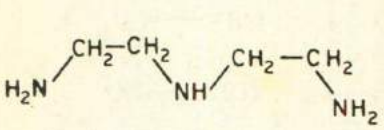
These ligands which "bite" at two positions in the metal ion are known as bidentate ligands. $\underset{\cdot\cdot}{N}H_2CH_2CH_2\underset{\cdot\cdot}{N}HCH_2CH_2\underset{\cdot\cdot}{N}H_2$ is a terdentate a ligand,

$$\underset{\cdot\cdot}{N}H_2CH_2CH_2\underset{\cdot\cdot}{N}HCH_2CH_2\underset{\cdot\cdot}{N}HCH_2CH_2\underset{\cdot\cdot}{N}H_2$$

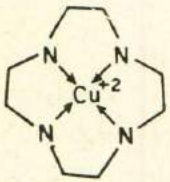
a quadridentate ligand

$$\begin{matrix}HOOCCH_2\\HOOCCH_2\end{matrix}\!\!>\!N\!-\!CH_2\!-\!CH_2\!-\!N\!<\!\!\begin{matrix}CH_2COOH\\CH_2COOH\end{matrix}$$

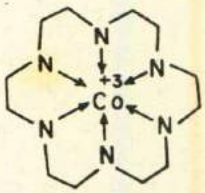
a hexadentate ligand (EDTA). The configuration of such chelate complexes are :



Tridentate Ligand



Tetradentate



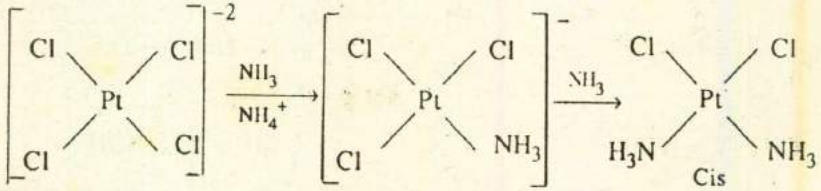
Hexadentate

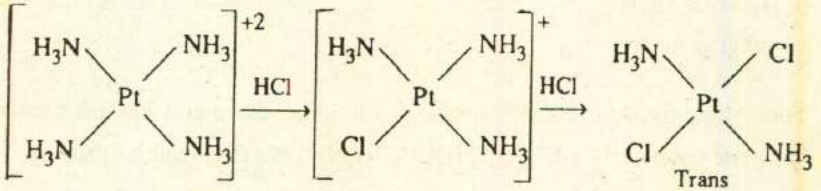
It is to be noted that tetradentate Cu-phathocyanine complexes assume square planar geometry imposed by the ligand structure.

Chelates in which both the coordination number and the oxidation number of the metal ions are satisfied simultaneously to produce neutral complexes, are often known as *Inner complex compounds.*

Cis-trans Configurations in Square Planar Complexes

Square Planar complexes may also exhibit cis-and trans-forms when unidentate ligands are used. $Pt(NH_3)_2Cl_2$ show cis-trans isomers which are determined by the method of synthesis.

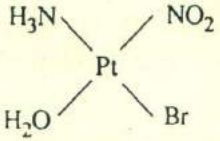




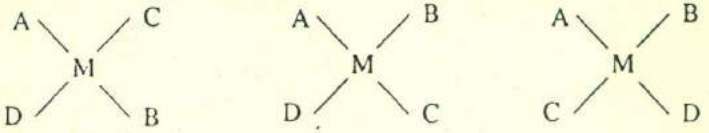
The synthesis is based on the principle known as *Trans Effect.* The trans effect is defined as the property of a ligand to direct an incoming ligand during the replacement reaction to take a position in the complex trans (opposite) to itself. Some of the ligands arranged in the decreasing order of the ability to function as trans eliminating group is as follows:

$CO \approx CN^- > NO_2^- > I^- > Br^- > Cl^- > NH_3 > OH^- > H_2O$

Application of the trans effect principle has made it possible to make complex species. Such as



This species is not optically active although there are four different ligands but it has three geometrical isomers.

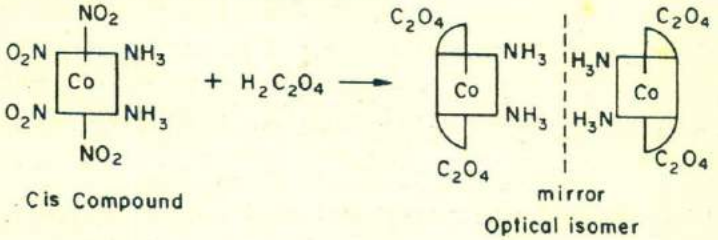


$A = NH_3$, $B = NO_2$, $C = Br$ and $D = H_2O$.

Cis-Trans isomers in simple complexes through chelation

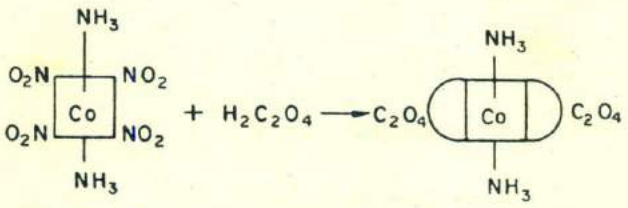
Optical activity in chelated complexes may also be used in connection with the determination of cis-trans isomers. The classical example of the cis-trans form of Erdmann's salt $NH_4[Co(NO_2)_4(NH_3)_2]$ which has both the cis-and trans-form configurations may be cited.

The conversion to oxalate complexes of the two forms leads to the introduction of metal oxlate complex ions.



Cis Compound

Optical isomer



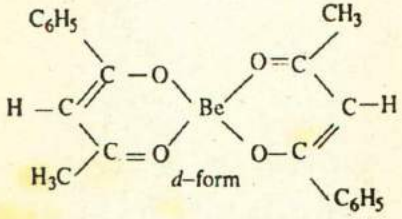
Trans-Compound

Symmetrical

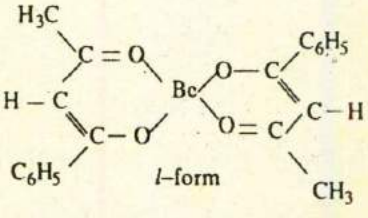
The trans form has mirror-images which are superimpossable and has no optical activity. But the cis-forms is optically active.

The mirror-image of cis-form is not supremipossable and therefore Erdmann's salt was proved to be a Cis-Compound. More examples have been given under chelate complexes.

Normally the tetrahedral arrangements of ligand give rise to the formation of optically active isomers. A unique case of optical isomerism occurs when 1-phenylbutan-1, 3-dione forms a complex with Be^{+2}.



d–form



l–form

In square planar complexes, no optical isomerism arises but an optically active ligand may impart optical activity in special cases.

METAL CARBONYLS

The transition metals having **d**-orbitals possess the ability to form compounds with various neutral molecules such as CO. These compounds of metals and CO are known as metal carbonyls. There are two groups of metal carbonyls namely (i) monometallic carbonyls such as $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$ etc and (ii) polymetallic carbonlys such as $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Co_2(CO)_8$, $Mn_2(CO)_{10}$ etc.

Preparation : These metal carbonyls are formed by various direct and indirect methods.

$$Ni + 4CO \xrightarrow[1\ atmos]{30—50°C} Ni(CO)_4$$

$$Fe + 5CO \xrightarrow[100\ atmos]{50°C} Fe(CO)_5$$

$$Co + 6CO \xrightarrow[200\ atmos]{100°C} Co(CO)_6$$

$$CoS + 8CO \xrightarrow[300\ atmos]{Cu\ or\ Ag} Co_2(CO)_8 \qquad X = halide$$

$$MX_n + yCO \xrightarrow[Pressure\ THF]{Tempr.} Mx\ (CO)y\ Xn \qquad M = metal$$

THF (tetra-hydrofurane) solvent

(unstable)
+ reducing agents
Ag, Na, Al, Mg etc.

$$\downarrow$$

$$Mx(CO)y$$

x = No. of metal atoms
y = No. of CO groups

$$Fe(CO)_5 \xrightarrow[photosynthesis]{uv\text{-}light} Fe_2(CO)_9 \longrightarrow Fe(CO)_5 + Fe_3(CO)_{12}$$

$$H_2Fe(CO)_4 \xrightarrow{MnO_2} Fe_3(CO)_{12}$$

$$HCo(CO)_4 \xrightarrow{heat} Co_2(CO)_8$$

Properties :

(a) Decomposed by heating giving very pure metals :

$$Ni(CO)_4 \xrightarrow{150^\circ} Ni + 4CO$$

$$Fe(CO)_5 \xrightarrow{heat} Fe + 5CO$$

(b) Act as reducing agent and react violently with O_2 or H_2O

$$Fe(CO)_5 + H_2O \xrightarrow{O_2} Fe_2O_3 + CO_2 + H_2$$

(c) No action of acids

(d) Reacts with NO and CO is replaced according to 3CO = 2NO

$$Cr(CO)_6 + 2NO \longrightarrow Cr(CO)_3(NO)_2 + 3CO$$

$$Fe(CO)_5 + 2NO \longrightarrow Fe(CO)_2(NO)_2 + 3CO$$

$$Co_2(CO)_8 + 2NO \longrightarrow 2Co(CO)_3\,NO + 2CO$$

(e) $Fe(CO)_5 + Ba(OH)_2 \xrightarrow[aq.\ soln.]{} H_2Fe(CO)_4 + BaCO_3$

(f) $Mn_2(CO)_{10} + 2Na \longrightarrow 2NaMn(CO)_5$

Structures of Metal carbonyls :

Lewis structure of CO is : C : : : O : and E. A. N. Rule is obeyed.

(i) E. A. N. for Metal Carbonyls:

Coordination with metals takes place through the lone pair of C. In many cases Effective Atomic Number Rule is obeyed in the cases of monometallic, polymetallic carbonyls, carbonyl hydrides and also carbonylate ions.

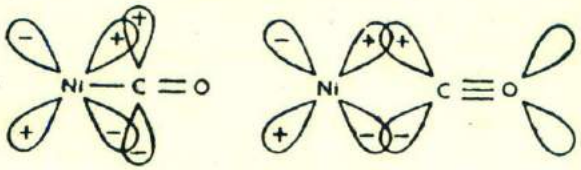
$Ni(CO)_4$ Ni = 28e + 4CO = 8e Total 28+8 = 36e (Kr)
$Fe(CO)_5$ Fe = 26e + 5CO = 10e Total 26+10 = 36e (Kr)
$Cr(CO)_6$ Cr = 24e + 6CO = 12e Total 24+12 = 36e (Kr)
$Mo(CO)_6$ Mo = 42e + 6CO = 12e Total 42+12 = 54e (Xe)
$W(CO)_6$ W = 74e + 6CO = 12e Total 74+12 = 86e (Rn)

It is to be noted that metal carbonyls contain metals in the zero oxidation states.

Odd atomic number metals carbonyls obey E. A. N. Rule in the ionic forms and in polymeric metal carbonyls, the metal-metal bonds satisfy the inert gas formalism :

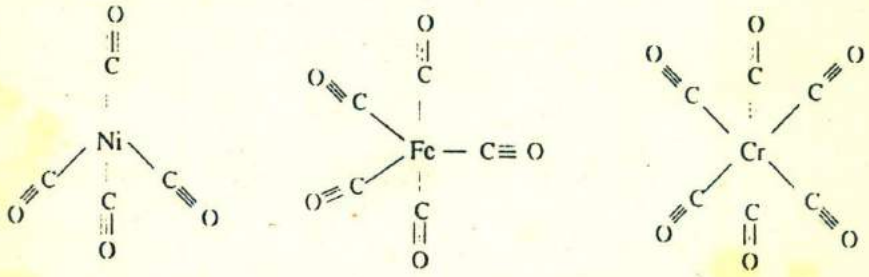
$Mn(CO)_5Cl$ Mn = 25e 5CO = 10e Cl^- = 1e Total = 36e
$Na[Mn(CO)_5]$ Mn = 25e 5CO = 10e + 1e Total = 36e
$H[Co(CO)_4]$ Co = 27e 4CO = 8e + 1e Total = 36e
$Fe_2(CO)_9$ 2Fe = 52e 9CO = 18e Fe—Fe = 2e Total 72/2 = 36e
$Co_2(CO)_8$ 2Co = 54e 8CO = 16e Co_2 = 2e Total 72/2 = 36e
$Fe_3(CO)_{12}$ 3Fe = 78e 12CO = 24e Fe_3 = 6e Total = 108/3 = 36e
$Co_4(CO)_{12}$ 4Co = 108e 12CO = 24e Co_4 = 12e Total 144/4 = 36e

(ii) *VBT and hybridization for Metal Carbonyls* : The metal-carbonyl bonds are linear and in monometallic carbonyls the formation of bonds occur due to hybridization of metal orbitals through overlap of d_π metal orbitals with p_π orbitals of CO and M—CO-bond. In $Ni(CO)_4$ metal uses sp^3 hybrid bonds giving tetrahedral geometry to the molecule. Similarly in $Cr(CO)_6$, chromium uses d^2sp^3 hybrid orbitals forming octahedral geometry of the

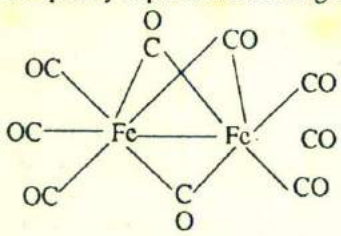


d_π - p_π bond. (VBT)

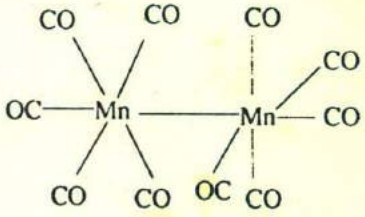
molecular structure. $Fe(CO)_5$ obviously is formed by the use of dsp^3 hybrid orbital of Fe (dz^2sp^3)



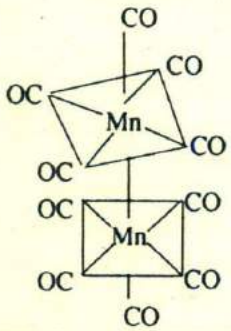
The polynuclear metal carbonyls contain metal-metal bonds which are not adequately explained according to Valence Bond Theory.



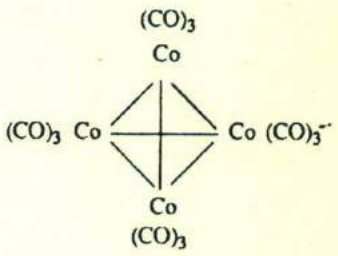
$Fe_2(CO)_9$



$Mn_2(CO)_{10}$

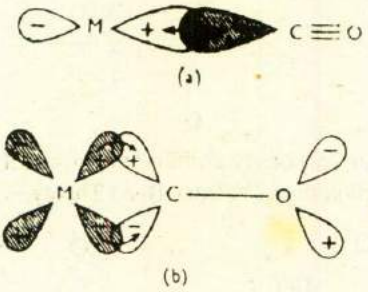


Tilted structure of $Mn_2(CO)_{10}$



$Co_4(CO)_{12}$

(iii) Structure of metal carbonyls according to Molecular Orbital Theory (MOT) : This is an elaborate treatment for bonding in metal carbonyls. The following points are taken into considerations: (i) C—O bond in CO (ii) metal-carbon bonds (iii) metal-metal bonds and (iv) bridging groups in polynuclear metal carbonyls. Firstly, there are triple bonds in CO having 1σ and 2π bonds. The carbon lone pair is actually hybrid sp bond. Secondly, the overlap of lone pair of carbon with d, s, p vacant metal orbital form metal-carbon bond. Thirdly, the C—M σ bond is further stabilized by back donation of π electrons from metal to C. This process takes place by the overlapping of filled non-bonding d orbitals of metal with the π^* antibonding orbitals of CO forming metal- ligand π-bonds.



(a) Overlap of metal orbital with filled σ-orbital of C giving M-C σ-bond. (b) Overlap of filled metal d_π or hybrid dp_π orbital with empty p_{π^*} antibonding orbital of CO.

Thus according to VBT, M—CO bonds in metal carbonyls are distinguished as C—M σ and M—C as d_π—p_π bonds, whereas MOT indicates C—M σ bond and M—C bonds are d_π—p_{π^*} (anitbonding orbitals of CO).

METAL NITROSYLS

Nitric oxide NO exists in three forms : NO, NO^+ and NO^-. Metal nitrosyls are the compounds of metals with the neutral NO which is coordinated to metal through N. The odd electron in NO in the antibonding orbitals is first transferred to the metal thereby reducing its oxidation number by one unit. NO^+ is isoelectronic with CO but coordinates with metals by donating 3 electron in the neutral form. Thus NO coordinates with metals to satisfy the need for an odd number of electrons for the E. A. N. rule. Therefore generally metal nitrosyls occur in complexes with mixed ligands.

$Fe(CO)_5 + 2NO \longrightarrow Fe(CO)_2(NO)_2 + 3CO$

$Co_2(CO)_8 + 2NO \longrightarrow 2Co(CO)_3NO + 2CO$

$Ni(C_5H_5)_2 + NO \longrightarrow C_5H_5NiNO$

$Cr(CO)_6 + NO \longrightarrow Cr(CO)_3(NO)_2$

NO^+ is isoelectronic with CO and CN^- and therefore mixed ligand complexes are formed as :

$K_2[Fe(CN)_5NO]$

$K_3[Fe(CN)_5CO]$

$K_4[Fe(CN)_5CN]$ i.e. $K_4[Fe(CN)_6]$

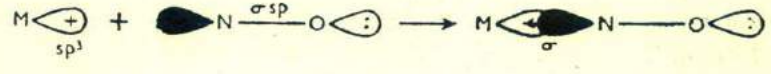
Nitroprusside ion $[Fe(CN)_5NO]^{-2}$ reacts with S^{-2} ion in alkaline medium to give violet colour used for identification of sulphides.

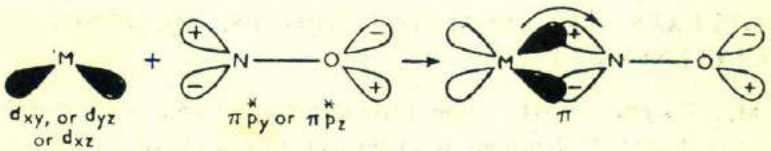
$$K_2[Fe(CN)_5(NO)] + S^{-2} + \text{alkali} \longrightarrow K_4\left[Fe(CN)_5\overset{\overset{O}{\|}}{\underset{\underset{S}{\downarrow}}{N}}\right]$$

Structure of metal nitrosyls : (i) NO transfers the odd electron to metal and the ligand NO^+ isoelectronic to CO coordinates with the metal. Hence NO is a 3 electron donor. Metal nitrosyls obey the E. A. N. rule as in the case of $Ni(CO)_4$, $Co(CO)_3(NO)$, $Fe(CO)_2(NO)_2$, $MnCO(NO)_3$ etc.

$$M + NO \longrightarrow M^- + NO^+ \longrightarrow M^{-2}-\overset{+}{N} \equiv \overset{+}{O} \longleftrightarrow M^-=\overset{+}{N}=O$$

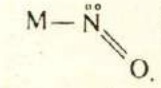
According to MOT, NO^+ is a σ– donor and back donation form metal to NO also occur. But π^*p_y and π^*p_z antibonding orbitals of NO^+ are empty and accept electrons from the metal d-orbitals. In the case of octahedral structure back





donation occurs from d_{xy}, d_{yz} and d_{xz} and in the case of tetrahedral the back donation occurs from $d_{x^2-y^2}$ and d_{z^2} metal orbitals.

(ii) The alternative assumption that NO first accepts an electron to form NO^- and then coordinates with an electron pair to the metal also holds good. Since apart from linear M—N=O bond system there are examples in which NO is bent.

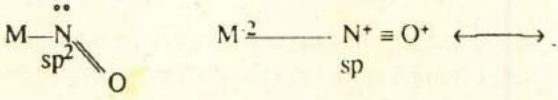


(N using sp^2 hybrid bonds)

Thus NO indicates anomalous behaviour.

Comparison of Metal Nitrosyls and Metal Carbonyls

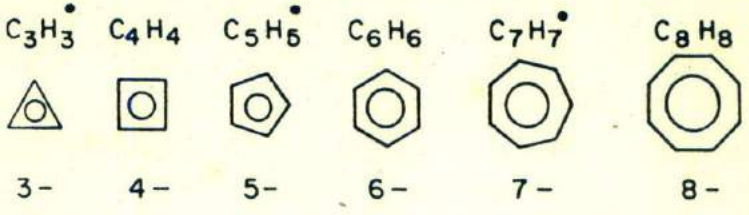
1. NO is a 3 electron donor. CO is a 2 electron donor.
2. 3 CO are replaced by 2 NO in a molecular structure
3. Both NO and CO give σ and π bonds with metals to form metal nitrosyls and metal carbonyls.
4. NO^+ is acidic but CO is neutral. Bonding of the two with metals appear to be complex.
5. CO always gives linear M—C ≡ O bonds. But M—N = O is also bent as well as linear



6. Substitution reactions occur in metal carbonyls but not in metal nitrosyls.
7. M—N bond is 1.57 – 1.67 Å whereas M—C bond is 1.7—1.9Å
8. Infrared absorption regions are different. (CO—1600 cm^{-1}, NO—1800 to 2300 cm^{-5})

COMPLEXES OF AROMATIC GROUPS. OLEFINES AND ACETYLENES

Metallocenes : C_5H_5 anion (cyclopentadienyl anion) derived from cyclopentadiene C_5H_6 functions as a uninegative ligand. Besides C_5H_6 a large number of carbocyclic systems and their derivatives give π-complexes with metals. The following are common π-complexes ligands.



π – ELECTRONS

The π-complexes of metals with C_5H_5 ion is generally called *Metallocenes*. The general formula is :

$$[(C_5H_5)_2 M^{n+}] X_{n-2}$$

where n = oxidation state of metal M and X is a uninegative ion such as Cl^-

Thus Fe^{+2} complex $Fe(C_5H_5)_2$ is known as Ferrocene

Ni^{+2} complex $Ni(C_5H_5)_2$ is known as nickelocene

Co^{+3} complex $Co(C_5H_5)_2Cl$ is known as dicyclopentadienyl cobalt(III) chloride. and so on.

Preparation : *1.* General method is the reaction of sodium cyclopentadienide with a metal halide or complex halide in suitable solvents such as tetrahydrofurane, ethylene glycol, dimethylformamide etc.

$$2C_5H_6 + 2Na \xrightarrow[\text{Ether}]{\text{THF or}} 2C_5H_5Na + H_2$$

$$\xrightarrow{\text{THF} \mid MX_2} M(C_5H_5)_2 + 2NaX$$

2. Direct reaction : When vapour of cyclopentadiene is passed over heated Fe at 300°C, ferrocene is produced.

$$2C_5H_6 + Fe \xrightarrow{300°C} (C_5H_5)_2 Fe$$

3. Grignard's reaction using cyclopentadienyl magnesium halide.

$$2C_5H_5MgBr + MX_2 \longrightarrow M(C_5H_5)_2 + MgX_2 + MgBr_2$$

$$C_5H_5MgI + FeCl_3 \longrightarrow Fe(C_5H_5)_2$$

Properties : (i) Complexes of first transition series Sc—Zn have all m. p. about 173°C. (ii) Vibrational spectra of the complexes resemble closely (iii)

M^{+3} complexes are strong electrolytes. (iv) These complexes are intensely coloured compounds.

Aromaticity : This is the property of a cyclic, conjugatively unsaturated molecule to undergo substitution reaction rather than addition reaction. Such substances are benzene and other such organic molecules, carboranes, phosphazines, carbocyclic ring metal π—complexes, etc.

Structures of Ferrocene

The peculiar structures were noted by the following reactions:

(i) $Fe(C_5H_5)_2$ could not be reduced by H_2 + a catalyst

(ii) $Fe(C_5H_5)_2 + KMNO_4 \longrightarrow$ No evidence of unsatruation

(iii) $Fe(C_5H_5)_2 + Br_2$ or $HNO_3 \longrightarrow [Fe^{+3}(C_5H_5)_2]^+$ Ferricinium cation.

(iv) Only one C—H stretching frequency in infrared spectra indicating all H are structurally similar and equivalent.

(v) Fe—C bond not localized to one C atom.

(vi) Multiple bonding occur between C rings and Fe due to donation of π-electrons to the vacant metal orbitals. But such donation is unlikely because of aromatic nature of the ring.

(vii) Donation of 6 electrons from each C_5H_5 - rings leads to d^2sp^3 hybrid bonds of Fe. This could not be proved by x-ray diffraction.

(viii) Significant Electron Number Rule (S. E. N.) indicated assumption of inert gas configuration by the metal atom in neutral condition for outer electron configuration such as :

$(C_5H_5)_2Fe$ Fe = 8e $2C_5H_5$ = 10e Total 18e (Ar)

$(C_5H_5)_2Co$ Co = 9 −1 = 8e $2C_5H_5$ = 10e Total 18e (Ar)

C_5H_5NiNO Ni = 10e C_5H_5 = 5e NO=3e Total 18e (Ar)

But not all fitted into the SEN rule.

$(C_5H_5)_2Ni$ Ni = 10e $2C_2H_5$ = 10e Total 20e

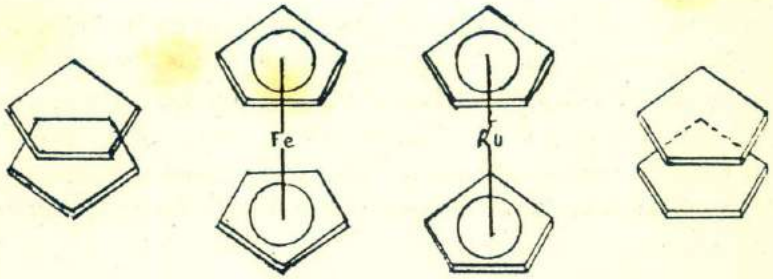
$(C_5H_5)_2Cr$ Cr = 6e $2C_5H_5$ = 10e Total 16e

$[(C_5H_5)_2Fe]^+$ Fe = 8 −1 = 7e $2C_5H_5$ = 10e Total 17e

E. A. N. Rule is not obeyed by these types of compounds.

(ix) Overlap may occur between two hybrid orbitals of metal atom with π orbitals of C_5H_5 rings. There are 5 M. O. for each ring with 6 electrons. 3 molecular orbitals are occupied by 3 pairs. The overlap of 3 filled M. O. of C_5H_5 rings with the vacant orbitals of Fe gives the bonding leading to Sandwich Bond.

Fe electrons are distributed as $d_{x^2-y^2}$ (2) d_{z^2}(2) d_{xy}(2), d_{yz}(1) and d_{xz}(1). The hybridization of d_{yz} and d_{xz} give cup-shaped molecular orbitals along z-axis. Sandwich bond is essentially one electron pair bond with $2C_5H_5^-$ rings with Fe^{+2}. The orientation of C_5H_5 rings may be staggrad or eclipsed :



staggard
Fe $(C_5H_5)_2$

eclipsed
Ru $(C_5H_5)_2$

It is to be noted that metal with d^{10} electrons do not give π- complexes but give σ complexes as in $Pb(C_5H_5)_2$.

$Mn(C_5H_5)_2$ does not give π complex but σ complex due to d^5 electrons according to Hunds' Rule.

Complexes of Olefins and Acetylenes.

Ethylene, propylene etc complexes are easily formed by absorption of the hydrocarbon in the metal halide solutions. Pd^{+2}, Pt^{+2}, Cu^+, Ag^+, Hg^{+2} absorb a variety of olefines and acetylenes. The general reaction :

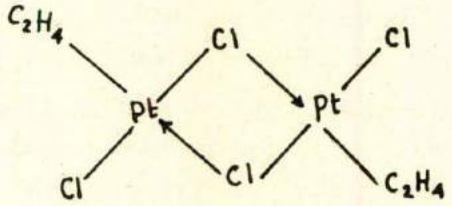
$$PtCl_4 + RCH = CH_2 \longrightarrow [PtCl_2.RCH = CH_2]_2$$

$$\downarrow$$

$$[PtCl_3\ RCH = CH_2]^-$$

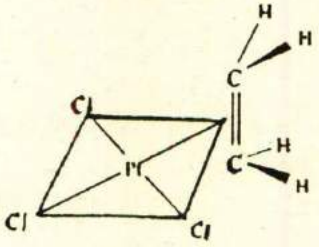
$$PtCl_4^{-2} + RCH = CH_2 \longrightarrow [PtCl_3\ RCH = CH_2]^- + Cl^-$$

$Pt\ Cl_2.C_2H_4$ is represented as a dimer.



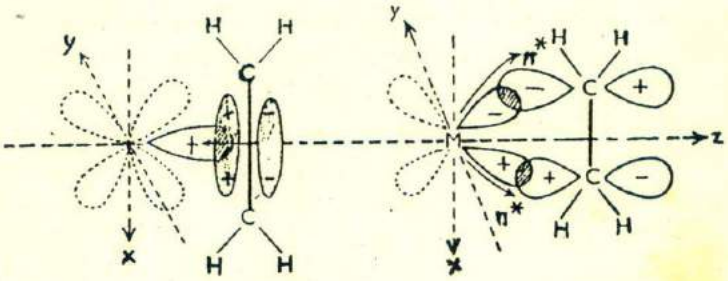
Dimer of $Pt\ Cl_2\ C_2\ H_4$

This instability of $[PtCl_2(C_2H_4)]_2$ is due to strong *trans effect* in substitution reaction. The type of bonds between the metal and the ligand appear to be quite complicated but it is clear that there is no localized σ bond between M and the ligand C (M—C bond). The bonding arises because of interaction of π electrons in the unsaturated molecule and hybrid orbitals of the metal. The double bond acts as a monodentate ligand and forms π bond with metals. Thus $K[PtCl_3C_2H_4]$ known as Zeise's salt has coordinated double bond perpendicular to coordination plane.



Anion $[C_2\ H_4\ Pt\ Cl_3]^-$ of Zeise's salt

Orbital overlap of C_2H_4 $2p_z$ orbital and **s, p** and **d** orbitals of metal is suggested involving no σ bonding.



(a) Donation from filled π-orbital to vacant metal dsp^2 orbital. (b) Back donation from filled metal dπ-pπ orbital to acceptor antibonding π^* orbital (π^*_z 2p) MO of C_2H_4.

Acetylene complexes are similar to those of ethylene and are formed with metals such as Pt, Cu etc. C_2H_2 has 2 π bonds at right angles to each other. In acetylide ion $[RC{\equiv}C]^-$ the complex formation is through the lone pair of electron. The acetylene complexes have complicated structure. The possibility of π bonding between metal and carbon in C_2H_2-complexes has been realized from the reactions with metal carbonyls.

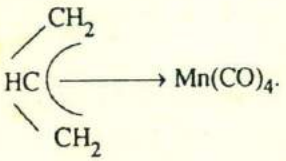
$Co_2(CO)_8 + RC{\equiv}CR \longrightarrow Co_2(CO)_6(RC{\equiv}CR) + 2CO$

Reaction of allylbromide with $NaMn(CO)_5$ also shows the π bonding

$$CH_2{=}CH{-}CH_2Br + 2NaMn(CO)_5 \xrightarrow{20°} CH_2 = CHCH_2\,Mn(CO)_5 + NaBr$$

$$\xrightarrow{80°} HC\begin{matrix}CH_2\\ \\ CH_2\end{matrix}\!\!>Mn(CO)_4 + CO + NaBr$$

The allyl group in this compound is symmetrical therefore, the actual molecular structure is represented as :



THE CRYSTAL FIELD THEORY (CFT) AND THE LIGAND FIELD THEORY (LFT) OF COORDINATION COMPOUNDS.

The basic principle of the crystal field theory is rather simple and depends on the factors : (1) shapes of the **d** orbitals, (2) the simple law of electrostatics that electrons or like charges repel each other. (3) The groups or ligands are considered as point charge of electricity.

It is necessary here to illustrate the potential energy diagram for the formation of a stable molecule through hybridized or excited state involving lowering of energy as given symbolically in Fig. 2—5 (Page 73). Similar situations arise during the formation of complex compounds when coordinating groups or *ligands* approach the **d** orbitals of the central metal ion. The influence of the charge clouds of the surrounding groups on the charge clouds of the metal ion (**d** orbitals) produces an electrostatic field known as the *crystal field.* The theory deals with this environmental electrostatic influence and is known as the *Crystal Field Theory.* The *Ligand Field Theory* is an extension of the Crystal Field Theory incorporating some aspects of the molecular orbital theory involving overlapping of orbitals.

The Octahedral symmetry

The five **d** orbitals which are degenerate (having the same energy) in the free metals ions have the shapes (boundary surfaces) with respect to x, y and z directions of Cartesian coordinates as given in Fig. 1—23 (page 54). Of the five **d** orbitals the $\mathbf{d}_{x^2-y^2}$ and $\mathbf{d}_{z^2}$ are directed along the axes x, y, and z whereas $\mathbf{d}_{xy}$, $\mathbf{d}_{yz}$, $\mathbf{d}_{xz}$ are directed in between (i.e., 45°) to the axes x, y and z. In an octahedral complex (6-coordinated complex) the ligands approach the metal ion along $\mathbf{d}_{x^2-y^2}$ and $\mathbf{d}_{z^2}$ orbitals as shown in Fig. 24-3. which are directed towards the ligands. The electrostatic repulsion raises the energy of these two **d** orbitals ($\mathbf{d}_{x^2-y^2}$ and $\mathbf{d}_{z^2}$) more than $\mathbf{d}_{xy}$, $\mathbf{d}_{yz}$ and $\mathbf{d}_{xz}$. Thus the **d** orbitals are split into two groups one of higher energy level comprising $\mathbf{d}_{x^2-y^2}$ and $\mathbf{d}_{z^2}$ (also represented as e_g) and the other of lower energy level $\mathbf{d}_{xy}$, $\mathbf{d}_{yz}$ and $\mathbf{d}_{xz}$ (also represented as t_{2g}). The stronger the field, the greater is the separation $10Dq$ between the energy levels.

This splitting ($10Dq$) of **d** orbitals lowers the total energy of the system thereby imparting stability to the new system as are illustrated in Fig. 24—4 The **d** orbitals of the ion in the field of spherical symmetry are split in an

octahedral field. The decrease in energy E caused by the splitting of d orbitals in presence of ligands is known as the *Crystal Field Stabilization Energy* (CFSE). or Ligand field Stabilization Energy (LFSE)

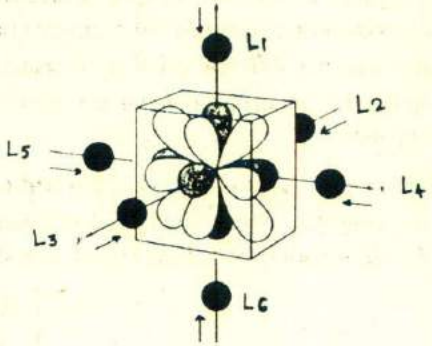


Fig. 24-3. 6 ligands approaching metal ion along dx^2-y^2 and dz^2 orbitals in octahedral complexes.

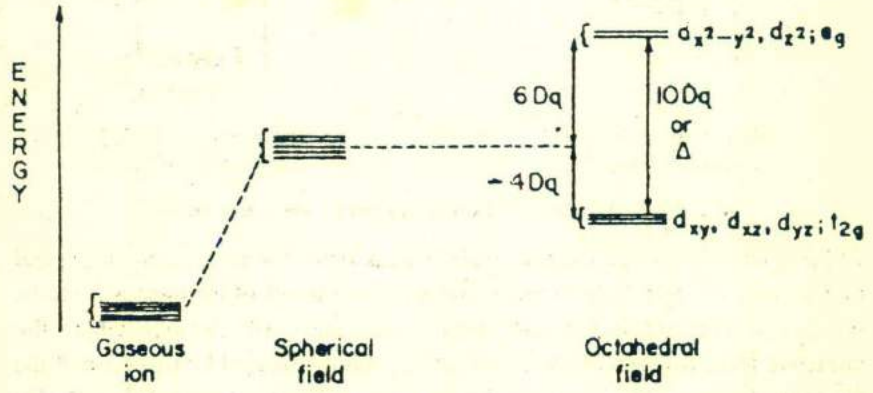


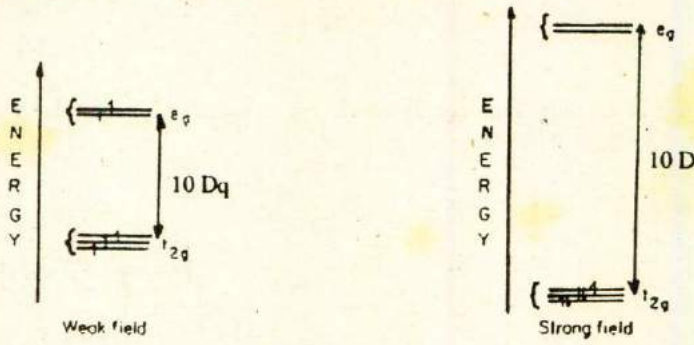
Fig. 24—4. Energy relationship of the formation of stable octahedral system by lowering of energy due to splitting of d orbitals.

Thus the splitting of d orbitals occurs because d-orbitals have different orientation in space and are subjected to different interactions by the approaching ligands. The splitting of the d-orbitals under the influence of ligand field

apparently depend on (i) charge or dipole of the ligand (ii) size and shape of the ligand (iii) number of the ligand (iv) polarisability (v) oxidation state of the metal (vi) variation in the d-orbitals (vii) ultimate geometry of the molecule.

The approaching ligands avoid areas of greater electron density and seek more comfortable positions with respect to the d orbitals of the metal ion. For this reason the complexes assume different geometrical shapes which thus depend on (1) the electrons in the d orbitals of the metal ion and (2) the strength of the field produced by the ligands.

Strong field produces pairing of electrons at lower d orbitals (t_{2g}) to give *Low Spin* form of the complex. Weak field produces more of unpairing of electrons and gives the *High Spin* forms of the complex as shown in Fig. 24-5.



High spin octahedral complex $[Fe(F)_6]^{-3}$

Low spin octahedral complex $[Fe(CN)_6]^{-3}$

Fig. 24–5. Splitting of d-orbital in strong and weak fields.

CFSE is large in strong field and small in weak field. The field strengths depend on the type, size and shape of the ligand and the distance of the ligands from the metal ion. The equilibrium internuclear distance is the position where the attractive force between the metal ion and ligand is balanced by repulsion of the electron-charge clouds. The crystal field splitting and electron distributions for octahedral $[Ni(NH_3)_6]^{+2}$, square planar $[Ni(CN)_4]^{-2}$ and tetrahedral $[NiCl_4]^{-2}$ complex ions are given in Fig. 24–6.

The Tetrahedral symmetry : This is closely related to the octahedral symmetry and contains four ligands arranged at the corners of a tetrahedron with the metal atom at the centre. The tetrahedral coordination is also closely related to the cubic system. The four ligands are situated at the alternate corners of the

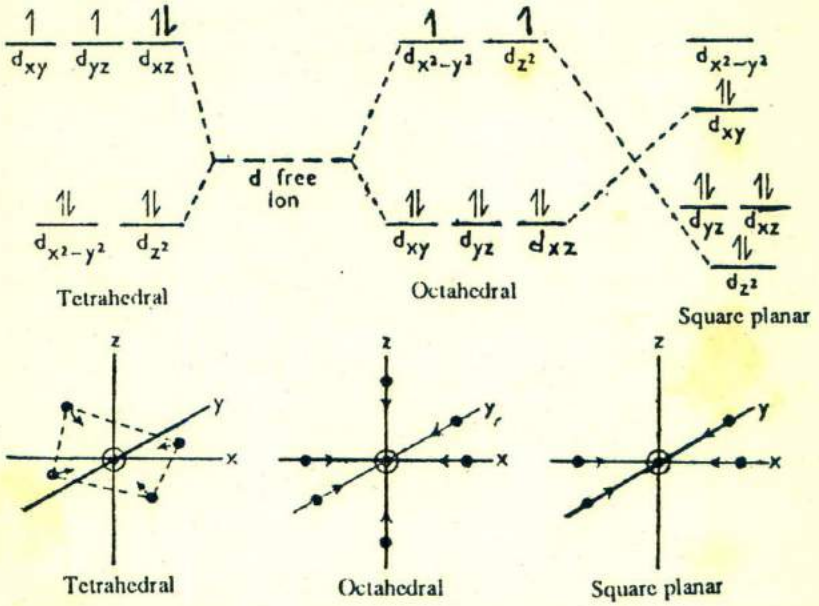


Fig. 24—6. Crystal field splitting in a tetrahedral $[Ni(Cl)_4]^{-2}$, octahedral $[Ni(NH_3)_6]^{+2}$ and square planar $[Ni(CN)_4]^{-2}$ complexes showing also the electron distribution (above).

cube. The orbitals which are directly affected on the approach of the 4 ligands are d_{xy}, d_{xz} and d_{yz}. Hence these orbitals are raised to higher energy level giving the splitting opposite to that of the octahedral symmetry as shown in Fig 24–7.

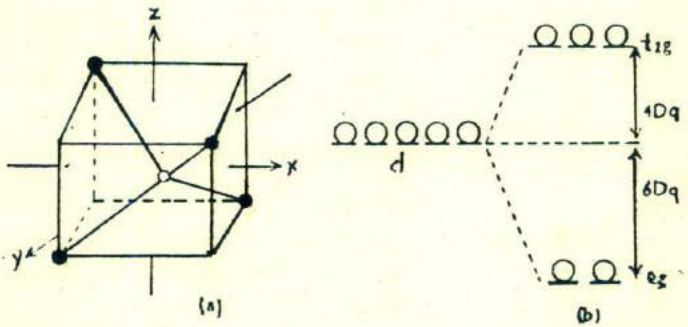


Fig 24–7. (a) Tetrahedral complex with ligands at alternate corners of a cube. (b) Splitting of the d- orbitals in tetrahedral field.

In this case the e_g orbitals are at lower energy and t_{2g} at higher energy. But the splitting in this case is less marked since the orientation of the d-orbitals produces smaller value of $10\,D_q$ so that

$$10\,Dq_{\text{tetrahedral}} = \frac{4}{9}\,10\,Dq_{\text{octahedral}}.$$

Tetrahedral Complexes are more common in the case of non-transition elements and for d^0, d^5 (high spin) and d^{10} ions. Due to smaller splitting of d-orbitals the tetrahedral complexes are always high spin form and no low spin form are observed in this geometry.

The Merits of the Ligand Field Theory :

(1) It gives clear understanding regarding the distortions in the geometry of the complex molecule.

(2) It explains the variations in the magnetic properties of the same metal ion in different compounds.

(3) It gives satisfactory explanations of the twin peaks observed when many physical properties of transition metal complexes of similar nature and compositions are plotted against the atomic numbers of the metals.

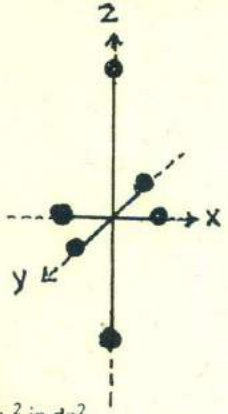
(4) It gives clear and quantitative understanding of the spectra of complexes.

(5) It gives general understanding of the structures of metal complexes in all states and forms, such as oxide systems.

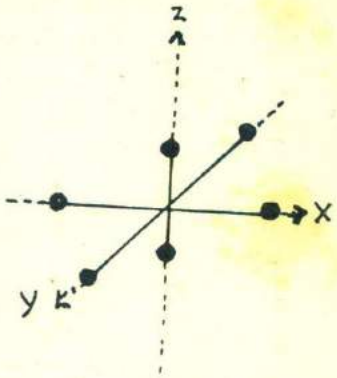
The Jahn-Teller Effect : The distortion in symmetrical structures due to partially filled energy levels is known as Jahn-Teller distortion. According to this concept the following points may be noted. (i) Any non-linear molecule having degenerate electronic system will be unstable. (ii) Such system becomes distorted to remove the degeneracy and lower the symmetry. (iii) The distortion splits the degenrate state and increases the stability of the molecule. (iv) The removal of degeneracy results in additional stabilization by lowering the energy.

The distortions (generally known as Jahn-Teller distortions) in complex compounds, such as those of Cu^{+2} ion having d^9 ion explain the defect of the valence bond approach. Cu^{+2} complexes have generally distorted octahedral structure. The splitting of the d orbitals of Cu^{+2} ion with 9 electrons gives two different distributions in the higher energy level (e_g) as shown in Fig 24—8. Cu^{+2} complexes have 4 short and 2 long bonds obviously due to the comfortable

approach of the ligands along x and y directions because of less electron density in $d_{x^2-y^2}$ orbital (one unpaired electron) as compared to two electrons (paired) in d_{z^2} orbitals which exerts greater repulsion to approaching ligands.



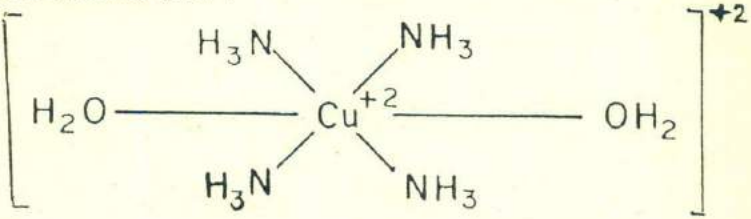
e_g^2 in dz^2
z-ligands moving out
(a)



e_g^2 in dx^2-y^2
z-ligand moving in
(b)

Fig. 24-8. The possible structures of $[Cu(NH_3)_4(H_2O)_2]^{+2}$ due to distortion in octahedral geometry.

The structure of $[Cu(NH_3)_4(H_2O)_2^*]^{+2}$ according to LFT is represented as tetragonal distortion as illustrated below :



In Fig. 24—8 two possible arrangements of d^9 complex ion give distorted octahedral structures. $[Cu(NH_3)_4(H_2O)_2]^{+2}$ has the structure (a) in which four bonds are closer to Cu atom and two bonds are far removed indicating the splitting having unpaired electron in $d_{x^2-y^2}$ orbital and not the structure (b) having the unpaired electron in d_{z^2}. The extent of olistortions in octahedral and tetrahedral geometries are given in Table 24.5.

The explanation of the twin peaks observed when a physical property of a similar series of the complex compounds is plotted against the respective atomic numbers is one of the important achievements of the Ligand Field Theory. Thus

Table 24.5 Jahn-Teller distortion due to d-electrons in octahedral and Tetrahedral system

Systems.	*Electron Configuration*		*Predicted distortions*
Octahedral	d^1, d^6	High spin	Tetragonal distortion (slight)
	d^2, d^7	"	Tetragonal distortion
	d^3, d^8	"	No distortion (ligand field effect only)
	d^4, d^9	"	Large distortion
	d^5, d^{10}	"	No distortion
	d^6	Low spin	No distortion
	d^8	"	Large distortion (square planar)
Tetrahedral	d^1 d^2 d^6 d^7	High spin	No distortion
	d^3 d^4 d^8 d^9	High spin	Large distortion

when the heats of hydration and stability constants of a series of complexes with the same ligand are plotted against atomic number from Ca (20) to Zn (30), as for $[ML_6]^{+2}$ complexes the curves obtained are given in Fig. 24–9.

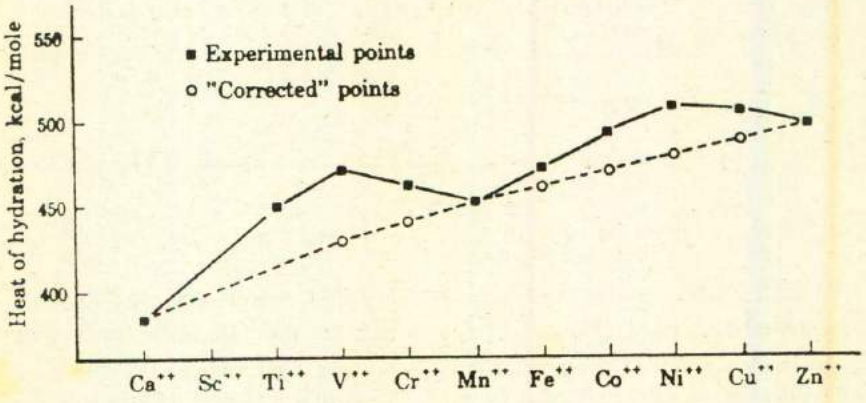


Fig. 24—9. Twin peaks in the case of heats of hydration or stability constant of complexes of M^{+2} transition metal ion such as $[M(H_2O)_6]^{+2}$ plotted against atomic number. In the absence of crystal field, the values would be expected to follow a regular increase as indicated by the broken lines.

For the divalent M^{+2} ions surrounded by $6H_2O$ molecules in solution the double peaks of the curve are due to the extra stability by the d electrons in the octahedral field. Notice that d^0, d^5 d^{10} ions do not show extra stabilization due to the symmetrical distribution. Similarly, the stability constant K of the complex equilibrium :

$$M^{+2} + 6L \rightleftharpoons [ML_6]^{+2}$$

is given by $K = \dfrac{[ML_6]^{+2}}{[M^{+2}][L]^6}$ where M^{+2} is a divalent metal ion and L is the ligand molecule, such as NH_3. When log K or log β is plotted against atomic number of M^{+2}, the curve obtained gives similar double peaks (Fig. 24–9). Without the concept of crystal field theory the values would be expected to increase regularly along a straight line.

Fig. 24–5 (page 726) gives an idea as to why the strong field of CN^- ion gives $K_3[Fe(CN)_6]$ in which the magnetic moment indicates the presence of a single unpaired electron whereas the weak field of F^- ion gives $K_3[Fe(F)_6]$ producing 5 unpaired electrons showing large value of magnetic moment.

In the complex of $[Ti(H_2O)_6]^{+3}$ there is only one d electron (d^1 ion). In the ground state this single electron occupies t_{2g} orbital. However, excitation of the electron to an e_g orbital is possible when energy required for the transition corresponding to the separation ($10Dq$) is supplied. The absorption of visible light brings about this transition. $[Ti(H_2O)_6]^{+3}$ absorbs most strongly at the wavelength of approximately 5000 Å (yellow region) or 20300 cm^{-1}. Due to a single unpaired electron, a single absorption band of the solution of $[Ti(H_2O)_6]^{+3}$ is obtained which spreads to a considerable portion of the visible spectrum. Thus the solution of $[Ti(H_2O)_6]^{+3}$ is violet-red because it absorbs yellow light (app. 5000 Å or 20300 cm^{-1}) but transmits the red and violet which are not absorbed as shown in Fig. 24—10.

The Spectrochemical Series : On the basis of the experimental studies on the spectral measurements of a large number of metal complexes with various ligands, it has been possible to arrange the ligands in the increasering or decreasing order of their ability to produce the ligand field splitting.

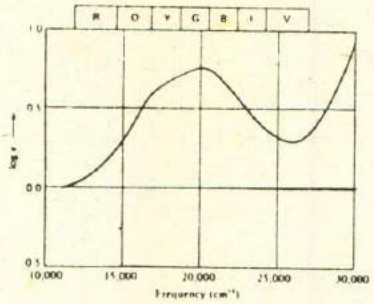


Fig. 24—10. The d—d transition (d^1 electron) in aqueous solutions of $[Ti(H_2O)_6]^{+3}$ ion giving violet-red colour of the solution. The curve on the right shows absorbance of yellow and transmission in the region of violet and red wavelength.

The arrangement of the ligands in the decreasing order or *vice versa* of the wave lengths corresponding to the splitting of the d-orbitals is generally known as the *Spectrochemical Series* of the ligands.

The series gives an idea of the splitting of the d-orbital under the normal conditions. The seriese in decreasing order gives some of the ligands of the series:

$CO > CN^- > NO_2^- > en > NH_3 > Py > NSC^- > H_2O > OH^- > F^- > NO_3^- > Cl^- > Br^- > I^-$

Thus the $10Dq$ values of some Ni–complexes are shown below :

Ligand	*10Dq in cm^{-1}*
Br^-	7000
Cl^-	7300
H_2O	8500
NH_3	10600
en	11200
O-Phen	12,700
CO	23000

It may be noted that both anhydrous $CuSO_4$ and $K_2[Cu(CN)_4]$ are colourless. SO_4^{-2} provides a very weak field and the d-d transition bands move into the infrared region. CN^- provides a very strong ligand field and d-d absorption bands occur in the ultraviolet region.

THE MOLECULAR ORBITAL THEORY (MOT) OF INORGANIC COMPLEXES

Molecular orbital theory provides an elaborate method for explaining the structures of inorganic complexes. The composite orbitals of the ligands are combined with the atomic orbitals of metal ions according to symmetry. Both bonding and antibonding orbitals are formed according to LCAO—MO. The MO treatment is highly mathematical and the building up of MO diagrammes for complexes are rather difficult. Only a simple pictorial representation are given here.

When a molecular orbital is formed in complexes the electrons from the metal ions and ligands first occupy the lowest energy molecular orbitals of the molecule and then progressively higher energy orbitals are filled up until the supply of electrons is exhausted.

Molecular orbital picture of complexes consists of both σ and π bonded groups. Examples of octahedral symmetry have the metal σ orbitals classified as:

p_x, p_y, p_z designated as t_{1u}
s designated as a_{1g}
dx^2-y^2 and d_{z^2} designated as e_g
The π orbitals involved are :
d_{xy} d_{yz} d_{xz} designated as t_{2g}
p_x, p_y, p_z designated as t_{1u}

The combination of atomic orbitals of metal ion with the Ligand Group Orbitals (LGO) may be represented pictorially as follows :

(1) The six LGO combine with s orbitals of metal to give 6 M—L σ bonds (Fig. 24–11).

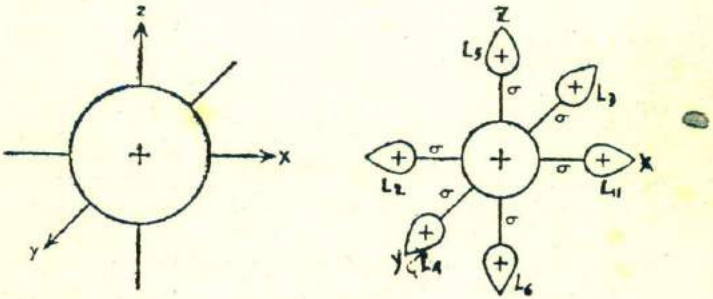


Fig. 24–11. Combination of s metal orbital with 6 LGO

(2) The $d_{x^2-y^2}$ and d_{z^2} orbitals combine with 4 LGO and 6 LGO respectively of the same symmetry (e_g) as in Fig 24–12)

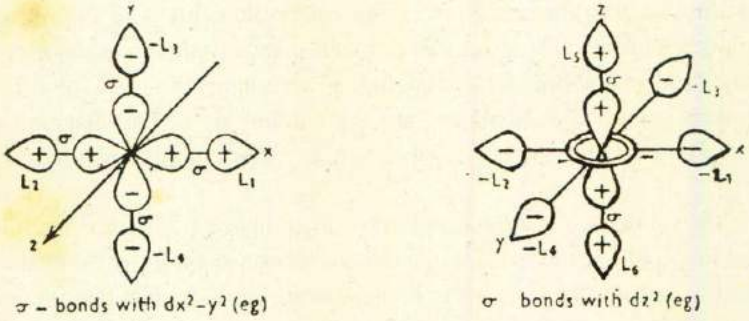


Fig. 24–12. Combination of dx^2-y^2 and dz^2 with ligands

(3) The p_x, p_y, p_z orbitals (t_{1u}) of metal overlap with the 6 LGO two for each p orbital (Fig 24-13)

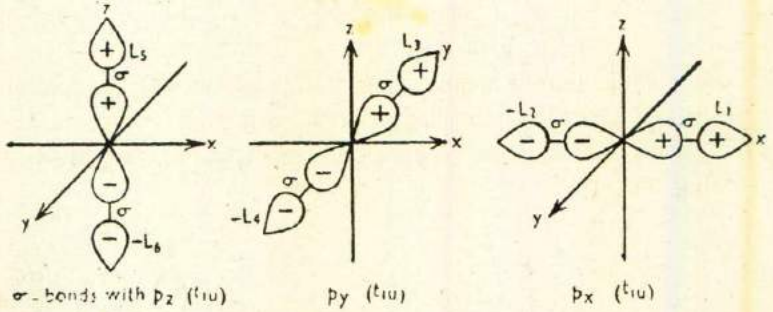


Fig. 24-13. Three p orbitals overlap with 6 LGO (two for each p)

The d_{xy}, d_{xz} and d_{yz} (t_{2g}) orbitals do not form σ- bonded complex.

The MO diagramme on the basis of calculation of energies based on Wolfberg-Helmholtz (WH) method gives the following picture of $[Ni(NH_3)_6]^{+2}$ complexes with σ bonds only as shown in Fig 24–14.

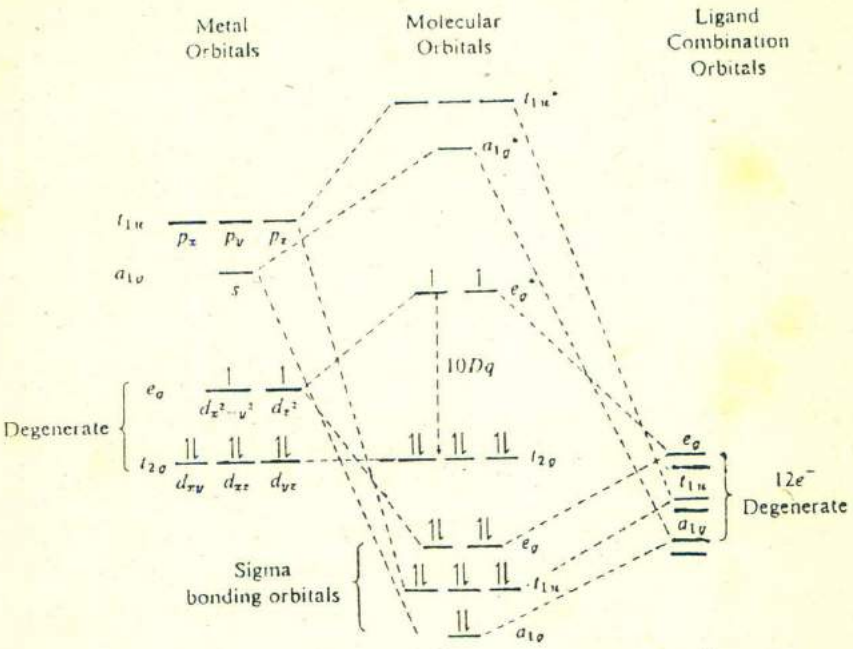


Fig. 24-14. MO diagram of $[Ni(NH_3)_6]^{+2}$ complex with σ bonds only.

Notice that the values of 10 Dq in terms of LFT and MOT are different.

LFT $10\,Dq = t_{2g} - e_g$, MOT $10\,Dq = t_{2g} - e_g^*$ (eg^*—antibonding molecular orbitals).

MOT and π Bonding Complexes

The t_{2g} metal orbitals are not always non-bonding but as in CN^- the π-orbitals has filled π bonding and also π^* orbitals. The ligand π orbitals may be simple $\mathbf{p}_\pi$ orbital as in Cl^- ion or simple $\mathbf{d}_\pi$ orbitals as in PH_3 or MO as in CO and CN^- ligands.

The metal $\mathbf{d}_{xy}$, $\mathbf{d}_{xz}$, $\mathbf{d}_{yz}$ may interact with $\mathbf{p}_x$, $\mathbf{p}_y$, $\mathbf{p}_z$ orbitals according to symmetry giving π_{xz}, π_{xy} and π_{yz}, orbitals. Similarly p—p interactions shall produce $\mathbf{p}_{\pi x}$, $\mathbf{p}_{\pi y}$ and $\mathbf{p}_{\pi z}$ molecular orbitals as shown in Fig. 24–15.

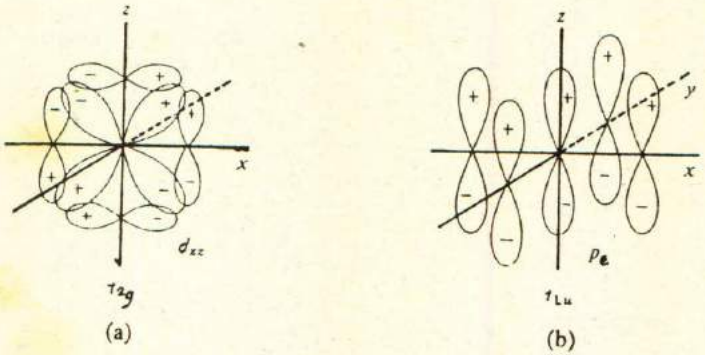


Fig. 24-15. (a) Interaction of d_{xz} with p_x and p_z orbitals of ligand giving π_{xz}. Similar interaction gives π_{xy} and π_{yz} (not shown). (b) Interaction of metal p_z orbital with ligand p_z orbitals. In all, $p\pi_z$, $p\pi_x$ and $p\pi_y$ are formed.

The resultant effect of π bonding shall be to increase the shifting of $10Dq$ or decrease it according to the ligand energies. π bonding effect of ligands of high energy shall increase the value of $10Dq$ from purely σ-bonded complex to have π-bonded effect as it happens in the cases of CO and CN^-.

But π orbitals of lower energy ligands than t_{2g} leads to the decrease of the splitting of $10Dq$ from σ bonded complexes having some π bonding effects as in the case of I^-, Br^- etc. shown in Fig 24–16.

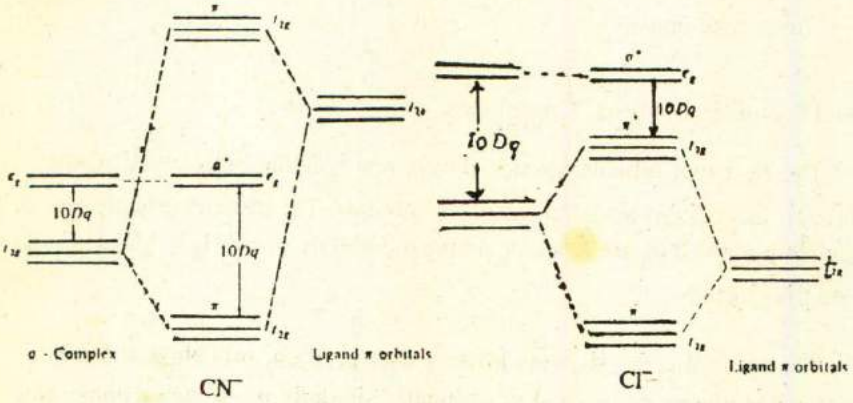


Fig. 2-16 Effects of π-bonding on the splitting of d-orbitals

Applications of Complex Compounds

Apart from the theoretical interests, the complex compounds have great importance not only in the field of chemistry but also in arts, industry and commerce. These have also great functional values in nature and biological functions. A few examples of the application of the complex compounds are given below.

In analytical chemistry, complex compounds are used more conveniently both for identification and quantitative determinations. Fehling solution, a tartrate complex of copper, is used to test for sugars, glucore and aldedydes in general. Dimethyl glyoxime provides a specific test for nickel and also gives an accurate method for its quantitative determination. Complexometric titrations using the complex disodium-EDTA (ethylenediamine tetra-acetic acid) have been largely used for the determination of calcium, magnesium etc.

Gold and silver are extracted from their ores by processes involving the formation of complex ions $Au(CN)_4^-$ and $Ag(CN)_2^-$. The complexes are also used in electroplating.

Complex compounds are used for dyeing fabrics which produces beautiful and fast colour due to the formation of complexes known as *lakes* with mordant dyes.

Beautiful paints and pigments used by the artists, consist of complex compound. In fact, the ink with which we write also consists of iron complexes.

From the point of view of a large number of application of complex compounds, these are substances of great commercial value.

Complex compounds occur in nature such as in blood (haemoglobin) which is an iron-complex and functions as the oxygen carrier of the blood stream. Similarly, the green colour of the leaves are due to magnesium complex of chlorophyll. Some vitamins such as B_{12} and enzymes consist of metal complexes.

Chelates are also used in medicines, drugs and treatment of diseases.

There are numerous applications of coordination complexes in industrial productions such as polymers, biochemical catalysis etc.

QUESTIONS AND PROBLEMS

1. Explain the bonding in $Co(NH_3)_6Cl_3$.
2. Write a short note on "Isomerism in 6-coordinated complexes".
3. Write note on the actions of ammonia on salts of mercury and silver.
4. Describe the reaction which occur when an aqueous solution of mercuric chloride is treated with an aqueous solution of potassium iodide.
5. Discuss the use of sodium cobaltinitrite in analytical chemistry.
6. Explain "Coordination compounds."
7. Cite some examples of the complex salts of chromium.
8. Explain the formation of coordination complexes according to VBT.
9. Describe what happens when ammonia is gradually added to an aqueous solution of $CuCl_2$.
10. Name a few complex compounds in which chromium shows σ-coordination number and give their structures.
11. Write a concise account of the Werner's theory of complex compounds.
12. Explain "Effective Atomic Number" and show how this idea explains the stability of some complex compounds.
13. Discuss Pauling's Valence Bond Theory to explain the structures of some complexes.
14. Make drawings to represent the structures of the following complex ions:—
    (a) $[Zn(NH_3)_4Cl_2]^{+2}$, (b) $[Cr(H_2O)_6]^{+3}$, (c) $[Ni(H_2O)_6]^{+2}$.
15. Discuss, with four examples, the uses of coordination compounds in analytical chemistry.
16. Write a note on Double salts and Complex salts.
17. What are coordination compounds ? Give the salient features of Ligand Field Theory.
18. Write brief accounts on :
    (a) Structure of metal carbonyls.
    (b) Inner complex salts.
    (c) Trans effect in 4 coordinated complexes.
19. Write a note on co-ordination bond.
20. (a) What is meant by "Coordination complexes"? Give three examples of such complexes.
    (b) Explain "Effective Atomic Number" and show how this principle explain the structure and stability of some complex compounds.

21. AgCl is soluble is soluble in ammonia but not in HCl. Explain.
22. Account for the existence of 2 and 3 forms of the following respectively : $Pt(NH_3)_2Cl_2$ and $[Pt(NO_2)(NH_3)BrCl]$
23. Write notes on :
    (a) Mond's process
    (b) Comparison of metal carbonyls and metal nitrosyls
    (c) Spectrochemical series of ligands.
24. H_2O coordinates with H^+ ion forming H_3O^+. Do you expect coordination of another H^+ ion forming H_4O^{+2}?
25. Discuss methods of identification of cis-trans isomers of inorganic complexes.
26. Draw sketches of 2 tetrahedral, 2 planar and 2 octahedral, coordination complexes.
27. Discuss the limitations of VBT involved in coordination compounds.
28. Discuss the structures of metal carbonyls.
29. Explain high spin and low spin inorganic complexes.
30. Explain the distortions of the geometry of metal complexes.
31. Write a note on Jahn-Teller Effect.
32. What are the effects of π-bonding on the splitting of d-orbitals during the formation of coordination complexes.

CHAPTER 25

SOLIDS, CRYSTALS AND CRYSTALLOGRAPHY

Polymorphism, allotropy and isomorphism :

The obvious properties of solids are their definite shape and size and rigidity. It is quite natural to suppose that the atoms and molecules in the solids have fixed positions and most of the space is occupied by the atoms themselves in contact with each other. Solids may be divided broadly into two groups :— (1) Crystalline solids, (2) Amorphous solids.

Crystals are solids having definite geometric shapes. The regular shapes of the crystals bounded by plane surfaces (called faces of the crystal) are due to the regular arrangement of the atoms in the crystal just like the arrangements of bricks in a wall. The order of arrangement of atoms in crystal in three-dimensions is so perfect that the position of each and every atom can be located if the positions of a few atoms are found out.

The faces of the crystals intersect at an angle characteristic of the substance. Thus sodium chloride forms cubic crystals and the faces of the cube in sodium chloride crystals intersect at a right angle (90°). When a crystal is broken it splits along certain preferred positions and the cleavage gives the characteristic faces and angles of the original form. *Cleavage* is thus splitting of the crystal along certain planes in which the binding forces are weak. The same crystalline state characteristics are retained even when the substance is ground to fine powder.

A particular substance may occur in different crystalline forms known as polymorphous. The phenomenon is known as *polymorphism*. Sodium chloride has cubic as well as octahedral crystalline forms. Ammonium nitrate occurs in five different crystalline forms.

When an element occurs in more than one crystalline form, it is said to have allotropic modifications and this phenomenon is called *allotropy*. Thus carbon occurs as diamond and graphite which are allotropic forms of carbon.

When a number of different substances have the same crystalline form, they are said to be *isomorphous* and the phenomenon is called *isomorphism*. Thus MgO and NaF are isomorphous substances.

Amorphous substances are those which do not have the ordered crystalline form. The atoms in such substances do not have orderly arrangements giving definite patterns. Thus glass is an example of amorphous solid. Even in some amorphous substances orderly arrangements are not lacking and polymers under certain conditions may consist of macromolecules or polycrystalline forms.

Anisotropy : It has been observed that the properties of a crystal are not the same in all directions. Many physical properties, such as solubility, magnetic susceptibility, thermal expansion, electrical conductivity etc. vary with the directions in the crystal. The variation of properties of a crystal in different directions is known as *anisotropy*. This phenomenon is exhibited because of the regular packing of atoms or molecules as shown in Fig. 25—1.

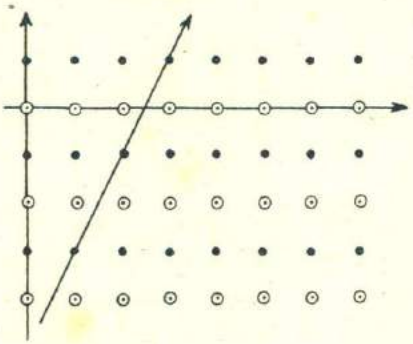


Fig. 25—1. Variation of properties of a crystal with the direction. Notice the different arrangements of points along the lines shown.

The constituent particles of a crystal are arranged in a repeating three-dimensional pattern. The pattern of points which describes the arrangements of molecules of atoms in a crystal in three-dimensions, is known as a *crystal lattice* or *space lattice*. The smallest portion of a crystal lattice which can be used to

describe the space lattice is called the *unit cell*. This is actually the repeat unit for the arrangement of atoms in the entire crystal structure. The two-dimensional crystal lattice and unit cell are shown in Fig. 25—2 (a).

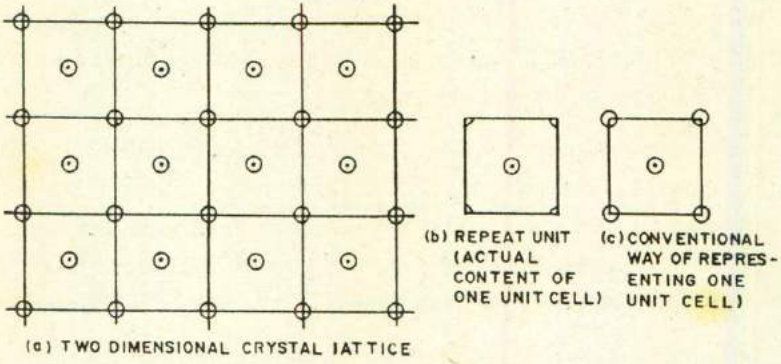


Fig. 25—2. Crystal lattice and unit cell.

It is observed that a group of repeat units combined together produce the two-dimensional pattern of the crystal lattice. The actual unit cell consists of four atoms at the corners and one full atom at the centre [Fig. 25—2 (b)]. But the conventional way of representing the unit cell is as shown in Fig. 25—2(c). The atomic surroundings at each corner of unit cell are identical. It may be noted that the pattern of crystal lattice can be divided into a sets of identical squares, rectangles or parallelograms constituting the unit cell. Any one of the possibilities may be chosen as the unit cell as shown in Fig. 25—3.

Types of Crystals

There are two different ways to classify crystals : (1) Classification on the basis of bonds between the units that occupy the lattice points and (2) classification according to the dimensions of the unit cell involving symmetry of arrangements.

Types of crystals on the basis of bonding system :

There are four types of crystals on the basis of bonding system : (1) Ionic, (2) Molecular, (3) Covalent and (4) Metallic.

In *ionic crystals* the units occupying the lattice points consist of positive and negative ions. Substances such as NaCl, MgO, CaS, Na_2SO_4 consist of

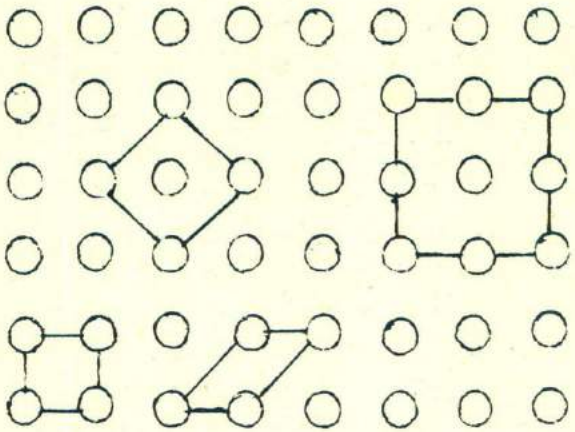


Fig. 25—3. Unit cell (4 different possibilities).

such units. The strong attractive forces between the positive and negative charges give solids of high melting point. They are brittle and show cleavage in definite directions and do not conduct electricity in the solid state but conduct electricity in the molten condition .

Molecular crystals consist of lattice points occupied by molecules. The fundamental building unit in this case is the molecule. The bonding with the molecule is covalent but the forces between the molecules give rise to the molecular crystals. The molecular forces are generally due to the dipole-dipole attraction or the van der Waals' attraction. These are weak forces and hence molecular crystals have low melting points and are soft because of easy displacement of the molecules from one position to the other. They do not conduct electricity. Ice (H_2O), gases in the solid state, iodine etc. are examples of molecular crystals.

The *covalent crystals* are those in which the shared electron-pair bonds combine all the atoms in the crystals into one giant molecule. The unit of structure is the atom. Thus in diamond every C atom is combined with all its nearest neighbours in three-dimension covalent bonds so that the bonding

extends throughout the whole crystal giving an interlocking structure. This arrangement gives the crystals the properties of hardness and high melting point. In quartz, Si and O atoms also form such a three-dimensional covalent crystal. Similar covalent crystals are formed in SiC, BN etc.

The *metallic crystals* consist of space lattice in which the unit is positive ion. The positive ions occupying the lattice point are immersed in a sea of highly mobile electrons of the valence shells. Metallic crystals are close-packed arrangements and generally belong to one of the three systems : *face-centred cubic*, *body-centred cubic* and *hexagonal close-packed*. The *electron gas*, or the sea of electrons belongs to the crystal as a whole. Because of the uniform charge distribution throughout the crystal lattice provided by the mobile electrons which also bind the positive metal atoms, the metallic crystals are good conductors of heat and electricity. These may be very hard as well as soft depending upon the forces of binding between the metal atoms in the crystals.

The different types of solid crystals on the basis of bonding systems are given in Table 25.1.

Table 25.1. Crystal lattices in terms of bonding.

	Types	*Unit of structure*	*Bonding system*	*Properties*	*Examples*
1.	Ionic	Positive and negative ions	Electrostatic attraction	Hard, brittle, high m. p., non-conductors	NaCl, K_2SO_4, MgO
2.	Molecular	Molecules	van der Waal's and dipole-dipole attraction	soft, low m. p., non-conductors	Ice (H_2O), Solid CO_2, I_2
3.	Covalent	Atoms	Shared electrons	Very hard, high m. p., non-conductors	Diamond (C), Carborundum (SiC), Quartz (SiO_2)
4.	Metallic	Positive ions in electron gas	Electrical attraction between + ve ions and electrons	Hard or soft, low m. p., high m. p., conductors	Na, Cu, Fe, Ag etc.

Types of crystals on the basis of unit cell symmetry :

Crystal systems are classified in terms of the dimensions of the unit cell along its three axes (a, b, c) and the three angles between the axes (α, β, γ). The relationships between the values of the angles and the relative lengths of the three axes form the basis for the classification of the solids into seven types of crystal systems. The crystals have the same symmetry as their constituent unit cells.

These seven types of crystal represent the simple or primitive types of space lattices. The unit cells of the seven crystal systems are given in Table 25.2 and illustrated in Fig. 25—4.

Table 25.2. Seven crystal systems on the basis of symmetry.

	System	*Axes*	*Angle*	*Examples*
1.	Cubic	$a = b = c$ (all equal)	$\alpha = \beta = \gamma = 90°$ (all 90°)	NaCl, CaO, Cu
2.	Tetragonal	$a = b \neq c$ (Two equal)	$\alpha = \beta = \gamma = 90°$ (all 90°)	MgF_2, MnO_2, Sn
3.	Orthorhombic	$a \neq b \neq c$ (different lengths)	$\alpha = \beta = \gamma = 90°$ (all 90°)	HgF_2, I_2, S
4.	Monoclinic	$a \neq b \neq c$ (different lengths)	$\alpha = \gamma = 90°$ $\beta \neq 90°$ (two 90°)	As_2S_3, B, S
5.	Triclinic	$a \neq b \neq c$ (different lengths)	$\alpha \neq \beta \neq \gamma \neq 90°$ (none 90°)	$CuSO_4 . 5H_2O$, CuO
6.	Hexagonal	$a = b \neq c$ (two equal)	$\alpha = \beta = 90°$ $\gamma = 120°$	SiO_2, AgI, C
7.	Rhombo-hedral	$a = b = c$ (all equal)	$\alpha = \beta = \gamma \neq 90°$ (equal but not 90°)	Al_2O_3, NiS, Bi

The seven different types of lattices have been obtained by considering the positions of the atoms at the corners of the unit cells. However, other types of lattices than the seven different types are possible and exist because the points may occupy positions in addition to the corners. Thus the cubic systems have three different lattices, e. g., simple cubic, body-centred cubic and face-centred cubic as shown in Fig. 25—5.

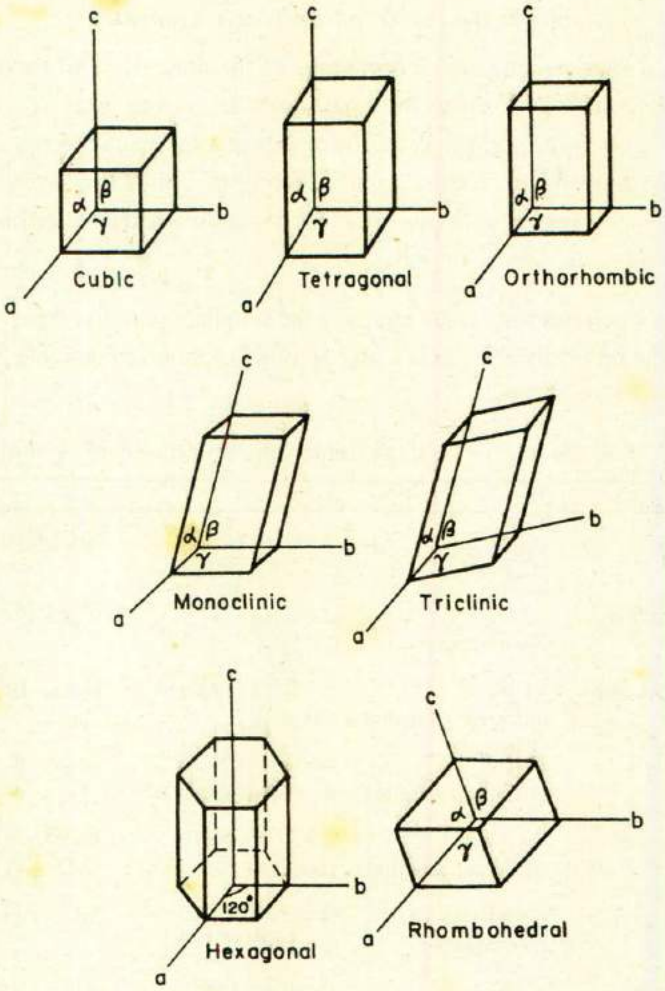


Fig. 25—4. The seven crystal systems.

Similarly, face-centred tetragonal and side-centred rhombic lattices also exist. Actually 14 distinct types of space lattices are recognised in which each point is surrounded in an identical manner by other points. These 14 space lattices are also known as Bravais Space Lattices. Further, this gives rise to 32 groups of symmetry known as *point groups* and 230 different kinds of three-dimensional arrangement of symmetry elements known as *space groups*.

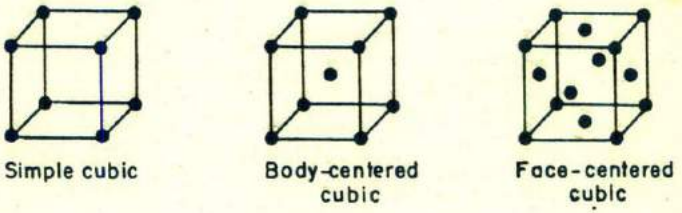


Fig. 25—5. The three different cubic lattices.

The points in the unit cell at the corners and other positions such as faces and centres represent positions occupied by an atom or a molecule.

Crystal symmetry and symmetry elements : The different types of symmetry formed in crystals are planes, axes and centre of symmetry. These are known as symmetry elements. *A plane of symmetry* divides the crystal by an imaginary plane into two parts which are mirror-images of each other in the plane. An *axis of symmetry* is an axis of revolution of the crystal which when operated makes the crystal present the same appearance more than once. The initial faces of the crystal may appear two, three, four or six times corresponding to rotation through 180°, 120°, 90° or 60° respectively as given in Fig. 25—6. A *centre of symmetry* is a point such that a line drawn through it intersects the crystal surfaces at equal distances on either side of the point.

Crystal coordination number : The unit cell in a crystal structure indicates the environment of an atom or molecule in a crystal. This environment gives the idea regarding the crystal structure when unit cells are joined together to form the lattice in three-dimensions. Coordination number in the crystal structure is the number of closest neighbours of the atom in a lattice.

Rational lines and planes : Considering the pattern of particles in two dimensions, as in Fig. 25—7, it is seen that a line AB, passing through a point in the lattice, will not necessarily pass through any other points. But the lines passing through two points must pass through an infinite number of points in the lattice as the lines XYZ and XPQ indicate. This is because such a line represents the side or diagonal of a square or a rectangle. These are called *rational lines*. In a three-dimensional lattice any plane passing through *three* points

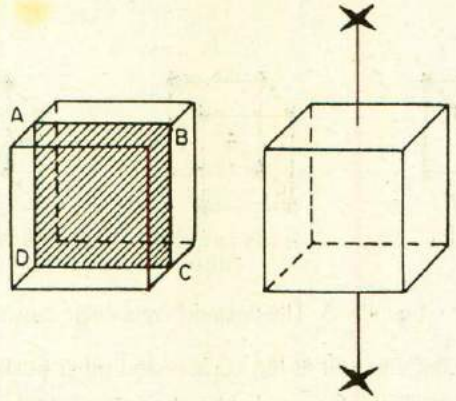


Fig. 25—6. An axis of symmetry and a plane of symmetry in a cube : (a) A plane of symmetry (ABCD) in a cube, (b) a four-fold axis of symmetry in a cube.

which are not in the same straight line will also pass through an infinite number of lattice points. These planes are called *rational planes*. Movement of the plane along the axes of the lattice by the unit-cell distance will give a number of parallel planes which will be separated from one another by equal distance which

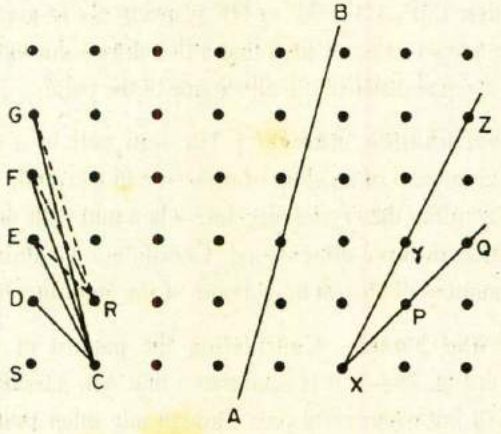


Fig. 25—7. Two-dimension rational lines.

is the same as that of the first plane from the lattice origin. This is illustrated in Fig. 25—8 with cubic lattices.

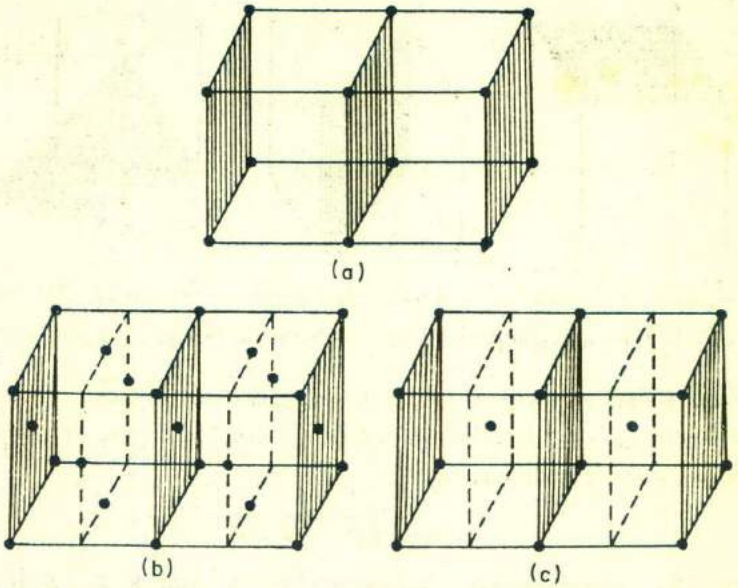


Fig. 25—8. Parallel planes passing through identical sets of points in (a) Simple cubic lattice, (b) Face-centered cubic lattice. (c) Body-centred cubic lattice.

In Fig. 25—7, showing the two-dimensional lattice, the lines CD, CE, CF and CG divide the horizontal line RD and all the lines parallel to it by 1, 2, 3 and 4 respectively. Similarly, the other pairs of lines CD and RE, CE and RF, CF and RG have the same intercept on the side of a unit cell. Since these lines are at equal distances in the lattice, the divisor or the intercept along base must be a whole number. In the same way the rational planes of three-dimensional lattice is identified by the divisor or intercept along each axis. The planes make intercepts with the three axis of the unit cell. The divisors or the intercepts are indicated by labels h, k, l and are known as the Miller Indices. Fig. 25—9 gives the values of h, k, l for the planes ABC. This plane at a unit distance from the origin O is designated as 1, 1, 1 plane or briefly written as (111). Similarly, other planes are designated as given in Fig. 25—9.

The distances between the similar parallel planes having identical arrangements of atoms are called *interplanar distances* or spacing distances of plane. This value is designated by the letter *d*.

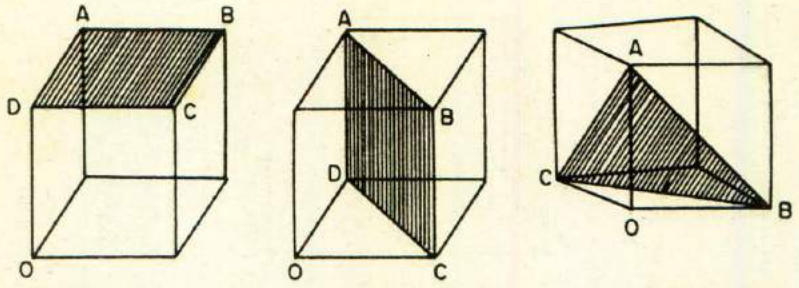


Fig. 25—9. Three different planes designated by Miller Indices in a cubic unit cell.

From simple geometry it can be proved easily that in a cube having the length of the side equal to a, known as *lattice constant*, the value of interplanar distances d is given by the equation :

$$a = d/\sqrt{h^2 + k^2 + l^2}$$

Table 25.3. Relationship between 'a', 'd' and h, k, l value of cubic crystals.

			Values of $h^2 + k^2 + l^2$ *for*				
hkl	$h^2 + k^2 + l^2$	*d*	*Simple Cubic*		*Body-centred Cubic*	*Face-centred Cubic*	
100	1	a	1	2	2		
110	2	$a/\sqrt{2}$	3	4	4	3	4
111	3	$a/\sqrt{3}$	5	6	6		
				8	8	8	8
200	4	$a/2$	9	10	10		
210	5	$a/\sqrt{5}$	11	12	12	11	12
211	6	$a/\sqrt{6}$	13	14	14		
				16	16		16
220	8	$a/\sqrt{8}$	17	18	18		
221 300	9	$a/3$	19	20	20	19	20

The possible values of the distances between atomic planes in cubic crystals may be calculated as given in Table 25.3. The values of $h^2 + k^2 + l^2$ indicate the crystal symmetry and planes of reflections. Knowing the values it is possible to identify the crystal symmetry from the systematic absences.

Determination of Structure

Crystallography is the study of solid substances for the determination of their identity and their crystal structure in terms of atomic configurations.

A great deal of informations about the internal structure of crystals have been obtained by X-ray diffraction experiments. X-rays are electromagnetic radiations of very short wavelengths. X-rays are generated by the impact of high-speed electrons from the cathode on a metal target (anode) in a vacuum tube (Fig. 25—10). The targets are generally copper, molydenum chromium, cobalt etc. The X-rays are directed at the sample crystals through a slit. The diffracted rays are recorded by a photographic film or other devices. The sample may be in the

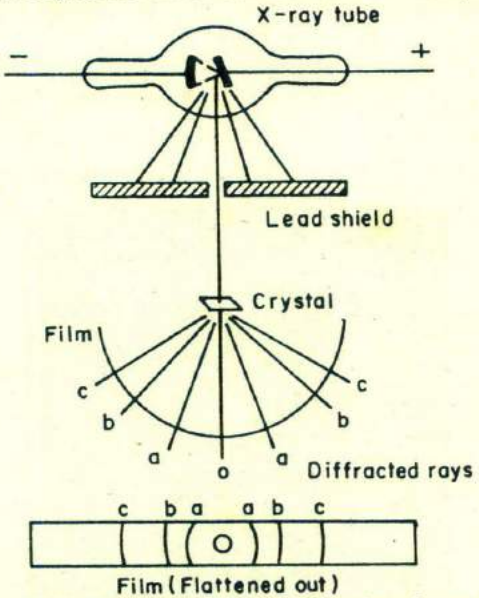


Fig. 25-10. Schematic of X-ray diffraction of crystals.

form of a single crystal or a large number of minute crystals (powder form). The diffraction of X-rays by crystals is similar to diffraction of ordinary light by a grating. The incoming X-rays interact with electrons that are present in the atoms of the crystals having a regular arrangements. The X-rays beam is scattered or deflected by the regular arrangements of atoms in the crystal. A photographic film is placed to record the scattered or deflected X-rays. On

developing the film a pattern is found which is characteristic of the structure of the crystals illustrated in Fig. 25—10. It is noted that in three-dimensional lattices a beam of X-rays striking one plane at angle permitting diffraction must strike all parallel planes having the same set of indices at the same angle and be diffracted similarly.

A monochromatic beam of X-rays is unlikely to hit a single and stationary crystal at all its planes. X-rays beam with a range of wavelengths is used or the single crystal is rotated or a large number of minute crystals (powder form) is used, so that a number of diffracted beams are obtained from the sample. The general techniques used to obtain an X-ray photographic pattern are : (1) Laue Method, (2) Powder Method and (3) Single Crystal Method.

Laue Method consists of obtaining X-ray photograph by using polychromatic X-ray beam on a single crystal. This method is no longer important and gives some information regarding the symmetry of the crystal structure. A sketch of the Laue pattern of NH_4Cl crystals is given in Fig. 25—11.

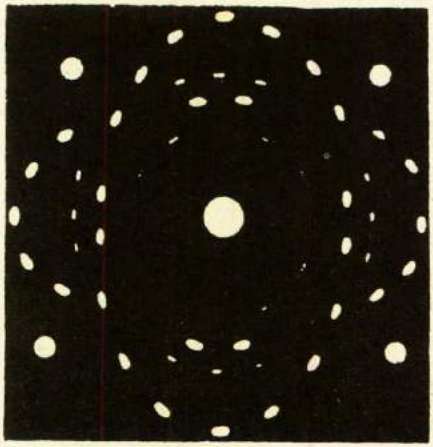


Fig. 25—11. A sketch of the Laue pattern of NaCl crystal.

The Powder Method employs monochromatic radiation with a large number of very small crystals (in the powder form) oriented at random. This is used chiefly for identification of crystalline substances and also to determine the structure in simple cases. A diffraction pattern by the powder method is given in Fig. 25—10 (bottom) when the film is flattened out.

The Single Crystal Method employs a single crystal of the sample which is rotated or oscillated on an axis perpendicular to the path of the incident X-rays of monochromatic radiation. When the developed film is flattened out a pattern as shown in Fig. 25—12 is obtained. This method is important for the determination of crystal structure. The crystal structure determinations have now been made fully automatic with the help of computers and applied for all types of extremely complex molecules (Fig. 25-14)

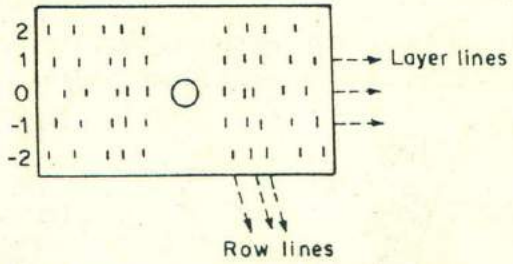


Fig. 25—12. Single crystal rotation pattern.

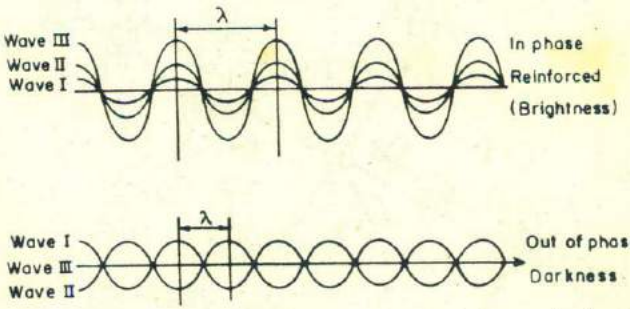


Fig. 25—13. Reinforcement of in-phase waves (top) and destructive interference of out-of-phase waves (bottom)

Origin of the Pattern

It has been mentioned that the diffraction of X-rays by crystal is similar to diffraction of light by a ruled grating which produces areas of brightness and darkness. The regular arrangements of atoms in space having the line of atoms in crystals also behave like tiny slits for the X-rays. Two waves that are in-phase reinforce each other and produce a resultant wave that has greater amplitude but the wavelength remains the same. Such waves produce areas of brightness. Two waves that are out-of-phase cancel each other by destructive interference. The resultant wave has no amplitude or intensity and produces areas of darkness. This

point is illustrated in Fig. 25—13 in which waves I and II give the resultant wave III.

A careful mathematical analysis of the patterns of the X-ray diffraction photographs gives the informations regarding the interplanar spacings (*d* values) and enables a crystallographer to calculate the positions of the atoms or molecules in the crystal which produces the pattern under examination.

Bragg's Equation

The basic relationship of the X-ray crystallography is given by the Bragg's equation. Considering that a beam of X-rays having single wavelength, λ, hits a

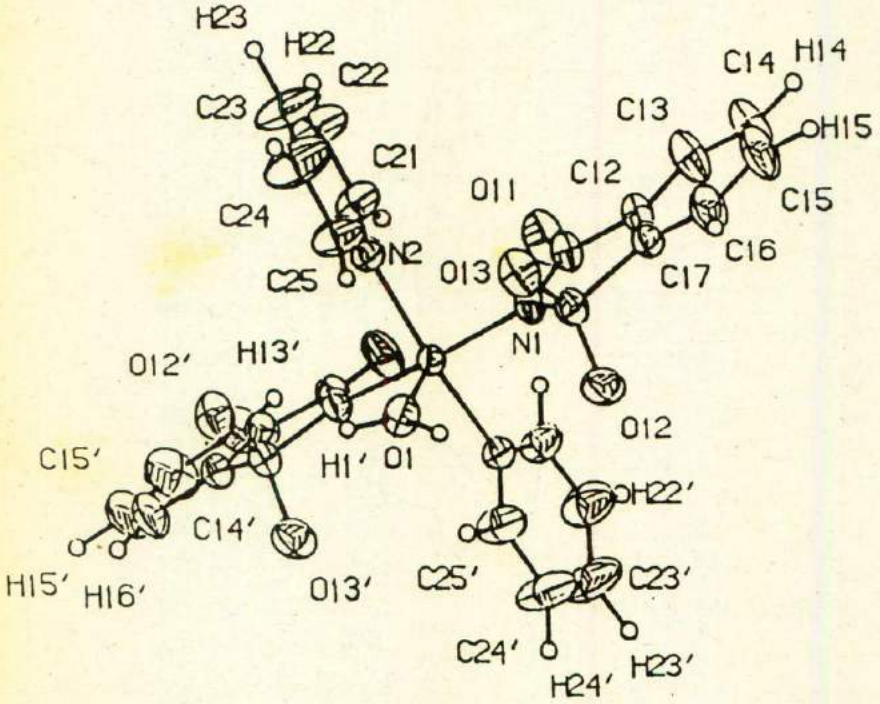


Fig. 25—14. Crystal structure of bis (sacaharinato pyridine) copper (II) hydrate $Cu(C_7H_4NO_3S)_2(C_5H_5N)_2H_2O$.

number of parallel planes of atoms within the crystal and taking only two such planes of atom the Bragg's equation can be easily derived as illustrated in Fig. 25—15. The wave-front AD approaches the two parallel planes xx and yy

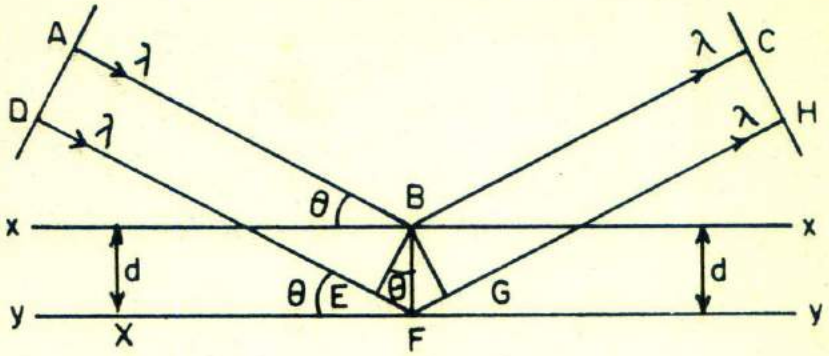


Fig. 25—15. X-ray diffraction from two parallel planes.

separated by the interplanar distance d, the angle of incidence is θ. Some of the rays are reflected from the upper plane and some from the second plane at points B and D respectively along BC and FH giving the reflection angle also equal to θ. A strong reflected beam will be produced only if the reflected rays are in-phase. It is seen from the illustration in Fig. 25—14 that path length of the ray DFH is greater than the path-length of the ray ABC by the distance EF + FG. These rays will be in-phase at CH only if the difference of path-lengths DFH–ABC (i.e., EF + FG) is equal to a whole number of wavelength $n\lambda$. Thus the condition for reflection of X-rays without destructive interference is

$$EF + FG = n\lambda$$

Angle BEF is 90° since BE is perpendicular to DF. Hence the sum of the angles EBF and EFB=90°. Angle XFB is 90° and angle XFE=θ. Therefore,

$$\angle EBF + 90° - \theta = 90° \text{ and hence } \angle EBF = \theta$$

Since $\sin EBF = \sin\theta = \frac{EF}{BF} = \frac{EF}{d}$

Therefore, $EF = d \sin\theta$

Similarly, $FG = d \sin\theta$

Therefore, $EF + FG = 2d \sin\theta$

or $n\lambda = 2d \sin\theta$

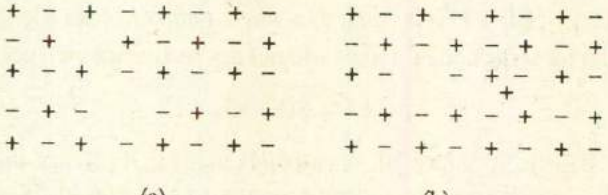
This is the Bragg's equation and may also be written as

$$\sin\theta = \frac{n\lambda}{2d}$$

Thus X-rays of definite wavelengths give reflections at various angles for a given set of planes with interplanar distance equal to d. These reflections correspond to $n = 1, 2, 3, 4$ etc. and are called *order of reflections*. As the order of reflection increases the angle also increases and the intensity of the reflected beam becomes weak. Thus the measurement of the angle at which diffraction occurs gives a method to calculate the distances between the planes of atoms within the crystal. It is to be noted that there are a number of interplanar spacings in a crystal corresponding to different sets of planes.

Defect structure : Examples of perfect crystals are not many. An ideal crystal is one which does not contain any *lattice defects* and can be completely described by the unit cell. There are several kinds of lattice defects.

Point defects are caused by missing ions giving *lattice vacancies* known as Schottky defect. The defects due to misplaced ions give *lattice interstitials* (Frenkel defect). In lattice vacancies, some of the lattice points are unoccupied, and in lattice interstitial, the atoms occupy positions between lattice points. Lattice defects in NaCl and AgBr are illustrated in Fig. 25—15.



(a) (b)

Fig. 25—15. Lattice defects : (a) vacancies in NaCl. Some of the Na(+) and Cl(-) ions are missing. (b) Misplaced Ag^+(+) in AgBr at interstitial site.

Distortion is the type of defect in crystal where planes of atoms are misaligned. The two types of distortion are known as *edge distortion* and *screw distortion*. Edge distortion results when a plane of atoms is inserted only partly into a crystal. Screw distortion has a line of atoms as an axis about which the crystal planes give the effect of screw threads.

The above-mentioned defects do not alter the stoichiometry of the crystal. But certain crystal defects arise due to *non-stoichiometry*. Thus a crystal of FeO contains more oxygen atoms than Fe atoms and ZnO contains more of Zn atoms to the extent of about 0.1%. The *non-stoichiometric* compounds contain extra

metal atoms or non-metal atoms in the interstitial positions between the ions of the crystals or they may occupy the ionic lattice positions. The structure as a whole is electrically neutral. The presence of impurities also imparts crystal defects. Mg^{+2} ion in NaCl gives rise to crystal defect. Similarly, As or B are added to Ge crystal to produce defect structures. Ge has the diamond structure but addition of B replaces a Ge (4 electron) atom with B (three electrons) atom. This gives rise to an electron hole. Similarly, an extra electron enters the structure of germanium by the substitution of an As atom (5 electrons) for a Ge. This type of defect due to the presence of impurities in crystal structure makes it conductor of electricity generally known as *semi-conductivity*. These materials are intermediate between conductors and non-conductors. Semiconductors differ from conductors in one important aspect. The conductivity of semiconductors is increased with the increase of temperature and also when the material is exposed to a beam of light. This is not observed in conductors. Hence semiconductors find applications as photocells, transistors and thermistors. Conductivity of the semiconductors are due to the motion of extra electrons or the existence of electron holes.

Certain optical properties, such as fluorescence and phosphorescence of some compounds, have been found to depend on the nature and extent of crystal defects. ZnS when precipitated from aqueous solution and dried at low temperatures does not show fluorescence upon exposure to ultraviolet light. But on heating ZnS to 900°C, the product contains a higher Zn/S ratio than that of ZnS. Irradiation of this ZnS to ultraviolet light produces an intense blue fluorescence. If the ignited ZnS contains 0.0001% CuS, the product gives a green fluorescence which persists after the source of radiation has been removed (that is, it also shows phosphorescence).

CHAPTER 26
NUCLEAR CHEMISTRY

The physical and chemical properties of all substances and the changes that these undergo from one form to another involve the electronic rearrangements of the atoms particularly the electrons in the outermost energy level. Nothing happens to the nuclei of the atoms during chemical reactions. Physical and chemical properties and reactions are, therefore, essentially associated with the electrons of the atoms.

However, a new type of transformation of matter involving changes in the atomic nuclei has attained tremendous advancement and has given rise to a new major branch of chemistry known as *Nuclear Chemistry.*

Nuclear Chemistry is the study of the properties, compositions and reactions of the nuclei of atoms.

In connection with the discovery of atomic nucleus it has been mentioned that certain elements, such as uranium, radium etc. undergo spontaneous disintegration to produce atoms of other elements together with radioactive rays. It is also seen that some elements are naturally radioactive such as uranium, thorium, radium, radon etc. but all others can be made radio-active by artificial means. The study of the chemistry of radioactive substances has given rise to the branch of chemistry known as *Radiochemistry.*

Radiochemistry is the study of the properties, compositions and reactions of radioactive elements and their compounds.

Nuclear chemistry thus embraces the study of radiochemistry which is a part of the general study of nuclear phenomenon. It may be noted that a very large number of isotopes occur in nature and can be made artificially which are not radioactive and can be studied by means of their nuclear properties other than radioactivity.

Discovery of Radioactivity

In 1985, Röntgen accidentally discovered X-rays which are able to penetrate materials that are opaque to light, produce ionization in their path, cause certain substances to emit light, and affect photographic films.

In 1896, the French scientist Becquerel discovered that uranium salt, such as potassium uranyl sulphate, $K_2UO_2(SO_4)_2$ gave out penetrating rays which affected a photographic plate wrapped in a black paper and kept in darkness. This seemed remarkable to Becquerel who observed that some X-rays like radiations must have been emitted by the chemical compound and penetrated through the black paper to affect the photographic plate even in the dark. Becquerel thus discovered an entirely new natural phenomenon that chemical substances spontaneously give out invisible rays which have properties like X-rays. These rays emitted by chemical substances are now known as *radioactive rays* and the phenomenon is known as *radioactivity*.

Thus radioactivity is the phenomenon of spontaneous production of invisible rays from chemical substances having the power of ionizing gas or air in its vicinity and affecting photographic plate or films.

Radioactive substances generally emit three types of rays :—

(1) **α- Rays** : These are helium-nuclei having charge + 2, (He^{+2}) and travel at a high speed. They are deflected from the straight path by a magnetic field or an electric field indicating positive charge. These rays have strong ionizing power but of short range.

(2) **β - Rays** : These are electrons having charge −1, (e^-) travelling at a very high speed. They are deflected by a magnetic field and also electric field indicating the negative charge. They are more penetrating than α- rays and ionize gases and have long range.

(3) **γ- Rays** : These are photons (units of radiant energy) and consist of electromagnetic radiation of very short wavelength like those of X-rays. They travel with the speed of light and have intense penetrating power. These rays carry neither mass nor charge.

Radioactivity is a nuclear phenomenon : Radioactivity is a nuclear property and is independent of the state of chemical combination or physical conditions. For example, a given quantity of radium has the same radioactivity regardless of whether the radium atoms are present in the metal, in solution, in solid salts or in the mineral. The radioactive rays emanate from the nucleus of the atom as it undergoes a process of spontaneous disintegration. When an atom emits α-or β-radiation, it becomes a new kind of atom. Due to the emission of α– particle from the nucleus, the mass of the nucleus is decreased by four units and the charge is decreased by two units. This happens because the loss of an α–particle is equivalent to the loss of 2 neutrons and 2 protons from the nucleus. The loss of 2 protons from the nucleus is accompanied by the loss of two planetary electrons whereby the electrical balance in the atom is retained. The spontaneous disintegration of the radium nucleus may be represented by the following equation :

$$_{88}Ra^{226} \rightarrow {}_{86}Rn^{222} + {}_{2}He^{4}$$

226 is the mass number and 88, the atomic number of radium. 222 is the mass number and 86, the atomic number of radon.

When a β- particle is ejected from the nucleus, a neutron in the nucleus evidently undergoes a transformation to give a proton and electron :

$$_{0}n^{1} \rightarrow {}_{1}p^{1} + {}_{-1}e^{0}$$

Due to the formation of a new proton at the expense of a neutron in the nucleus, a net increase in the positive charges takes place, as a result the atomic number of the new elements is increased by one unit. The expulsion of a electron from the nucleus does not affect the mass of the nucleus. This is illustrated when an isotope of thorium changes to protoactinium:

$$_{90}Th^{232} \rightarrow {}_{91}Pa^{232} + {}_{-1}e^{0}$$

The emission of an α– or β- particle may be accompanied by γ-radiation. The emission of γ-rays does not change the atomic number or the mass number of an atom because γ-rays possess neither mass nor charge.

The above observations together with the experimental determination of the rate of disintegration and half-lives of radio-elements (a characteristic property

described later) led scientists to conclude that radioactivity is a nuclear property. The radioactive disintegration takes place in the nucleus of an atom. α-particles with mass 4 and charge +2 could come out only from the nucleus which contains the mass and positive charges. The change in atomic number does indicate that β-particle must come from the nucleus. The loss of a unit negative charge increases the positive charge on the nucleus through neutron to proton conversion mechanism involving loss of β-rays known as β-decay.

Group Displacement Law

The emission of α–and β–particles from atomic nuclei obviously give rise to displacement in the positions of the product of disintegration in the Periodic Table because of the change of the atomic number of the parent element. These displacements are described by the so-called *Group Displacement Law*:

(1) When an element gives out an α-particle, the product obtained moves two positions lower than the parent element in the Periodic Table (atomic number decreased by 2). Mass of the element is decreased by 4 units.

(2) When an element gives out a β-particle, the product obtained moves one position higher than the parent element in the Periodic Table (atomic number increased by 1). Mass of the element remains the same.

Elements undergoing successive disintegrations and producing a number of elements which are radioactive isotopes give rise to a chain of species known as *radioactive series*. There are three different radioactive series of elements which are of natural origin and include most of the natural radioactive elements of the Periodic Table. Besides there is the fourth series discovered during World War II. This series is called the Neptunium series which was discovered by the production of the series members by artificial means. Thus there are four radioactive series, namely :

(1) The Uranium series,

(2) The Actinium series,

(3) The Thorium series,

(4) The Neptunium series.

Each series is characterized by a parent (first element) of long life and the ultimate end product leads to a stable isotope which is not radioactive. The

various series consisting of transformation from the parent element to the end product of stable isotopes are outlined as follows:

The Uranium series	The Actinium series	The Thorium series	The Neptunium series
$_{92}U^{238}$	$_{92}U^{235}$	$_{90}Th^{232}$	$_{93}Np^{237}$
$\downarrow\alpha$	$\downarrow\alpha$	$\downarrow\alpha$	$\downarrow\alpha$
$_{90}Th^{234}$	$_{90}Th^{231}$	$_{88}Ra^{228}$	$_{91}Pa^{233}$
$\downarrow\beta$	$\downarrow\beta$	$\downarrow\beta$	$\downarrow\beta$
$_{91}Pa^{234}$	$_{91}Pa^{231}$	$_{89}Ac^{228}$	$_{92}U^{233}$
$\downarrow\beta$	$\downarrow\alpha$	$\downarrow\beta$	$\downarrow\alpha$
$_{92}U^{234}$	$_{89}Ac^{227}$	$_{90}Th^{228}$	$_{90}Th^{229}$
$\downarrow\alpha$	$\alpha\swarrow\searrow\beta$	$\downarrow\alpha$	$\downarrow\alpha$
$_{90}Th^{230}$	$_{87}Fr^{223}$ $_{90}Th^{227}$	$_{88}Ra^{224}$	$_{88}Ra^{225}$
$\downarrow\alpha$	$\beta\searrow\swarrow\alpha$	$\downarrow\alpha$	$\downarrow\beta$
$_{88}Ra^{226}$	$_{88}Ra^{223}$	$_{86}Rn^{220}$	$_{89}Ac^{225}$
$\downarrow\alpha$	$\downarrow\alpha$	$\downarrow\alpha$	$\downarrow\alpha$
$_{86}Rn^{222}$	$_{86}Rn^{219}$	$_{84}Po^{216}$	$_{87}Fr^{221}$
$\downarrow\alpha$	$\downarrow\alpha$	$\downarrow\alpha$	$\downarrow\alpha$
$_{84}Po^{218}$	$_{84}Po^{215}$	$_{82}Pb^{212}$	$_{85}At^{217}$
$\downarrow\alpha$	$\downarrow\alpha$	$\downarrow\beta$	$\downarrow\alpha$
$_{82}Pb^{214}$	$_{82}Pb^{211}$	$_{83}Bi^{212}$	$_{83}Bi^{213}$
$\downarrow\beta$	$\downarrow\beta$	$\downarrow\beta$	$\downarrow\beta$
$_{83}Bi^{214}$	$_{83}Bi^{211}$	$_{84}Po^{212}$	$_{84}Po^{213}$
$\downarrow\beta$	$\downarrow\beta$	$\downarrow\alpha$	$\downarrow\alpha$
$_{84}Po^{214}$	$_{84}Po^{211}$	$_{82}Pb^{203}$	$_{82}Pb^{209}$
$\downarrow\alpha$	$\downarrow\alpha$	(stable)	$\downarrow\beta$
$_{82}Pb^{210}$	$_{82}Pb^{207}$		$_{83}Bi^{209}$
$\downarrow\beta$	(stable)		(stable)
$_{83}Bi^{210}$			
$\downarrow\beta$			
$_{84}Po^{210}$			
$\downarrow\alpha$			
$_{82}Pb^{206}$			
(stable)			

It may be noted that expulsion of one α-particle from an element and subsequent expulsion of two β-particles bring the element back to the same position in the Periodic Table thus giving rise to an isotope which are elements having the same atomic number.

It is to be remembered that in general, γ-rays are emitted each time the atomic nuclei undergo disintegration. The disintegration of uranium stops with the formation of lead 206. Samples of lead occurring in nature and from different radioactive minerals have different atomic weights. The actinium series starting from $_{92}U^{235}$ and the thorium series starting with $_{90}Th^{232}$ both also end with the formation of lead as the end product giving isotopes $_{82}Pb^{207}$ and $_{82}Pb^{208}$ respectively. Thus natural lead is a mixture of four isotopes having mass number 206, 207, 208 and 209. The proportions in which these isotopes are present give natural lead (Pb) its atomic weight of 207.21. This happens in the case of all elements. Recently the fourth radioactive series known as the neptunium series was discovered. $_{93}Np^{237}$ is the longest lived member which is the starting element and the series end at $_{83}Bi^{209}$ which is the stable product.

Radioactive Equilibrium

It may also be noted that the rate of disintegration of all the radio-elements are not the same. Some element, such as U^{238}, disintegrates very slowly whereas Ra disintegrates rapidly. Those radio-elements which are decaying at a rapid rate are also produced by their predecessor exactly at the same rate in nature. Hence they can not disintegrate out of existence because the parent element is producing the element at the same rate at which it is disintegrating. Such condition is known as *radioactive equilibrium* and is not reversible as in the case of chemical equilibrium which is a reversible phenomenon. Thus if an element A changes to B which again changes to C, then B will be at radioactive equilibrium if the rate of change of A to B, i. e., dA/dt (disintegration of A) and the rate of change of B to C, i. e., dB/dt (disintegration of B) are the same.

$$\text{If } A \rightarrow B \rightarrow C, \text{ then } \frac{dA}{dt}. = \frac{dB}{dt}$$

Disintegration or Decay Constant

The rate of disintegration of a radio-element is absolutely independent of all physical or chemical factors and is also different for different elements. Experimentally it has been found that every radioactive disintegration occurs at a rate that is directly proportional to the quantity of disintegrating material present. Hence the rate of disintegration of a radio-element follows the first-order reaction. Thus we have the following statement.

The rate of disintegration of a radioactive element at any time is proportional to the number of atoms of the element present at that time.

Let N be the number of atoms present at time t. If in the small interval of time dt the number of atoms which disintegrates is dN, then the rate of disintegration is $-\frac{dN}{dt}$ (minus sign indicates decrease in amount with time). Since the rate of disintegration is proportional to N (total quantity of radio-element), therefore, we have :

$$-\frac{dN}{dt} \propto N$$

$$\text{or} -\frac{dN}{dt} = \lambda N$$

where λ is a constant called Decay Constant or Disintegration Constant. When the rate of disintegration in unit time (per second) is taken into account, i.e., when dt = 1 second, we have,

$$-dN = \lambda N$$

$$\text{or } \lambda = -\frac{dN}{N}$$

Hence λ, the Decay Constant, is defined as the *fraction of the total number of atoms of the radio-element disintegrating per second. This has a characteristic value for each radioelement.* But the most important characteristic property of a radio-element is generally considered to be its half-life. Very often reference is made to the half-life of radioactive element which actually determines the radioisotope.

Half-life of Radio-elements

The *half-life* of a radioelement is the time required for one-half of the atoms in a sample to disintegrate.

Since the amount of the radioactivity is directly proportional to the quantity of radio-element (number of atoms of radioelement) the definition for half-life can also be stated as : The time required for a radio-element of a given amount to lose 50% of its activity. Integrating the equation

$$-\frac{dN}{dt} = \lambda N, \quad \text{i. e.,} \quad -\frac{dN}{N} = \lambda dt$$

between time interval zero to any time t. We have, $\int_0^t -\frac{dN}{N} = \int_0^t \lambda dt$

$$ln N_t - ln N_o = \lambda t$$

$$\text{or exponentially } \frac{N_t}{N_o} = e^{-\lambda t}$$

Where N_t = the number of atoms present at time t.

N_o = the number of atoms initially present, when t = 0

At half-life, $t_{1/2}$ we have $\frac{N_t}{N_o} = {}_{1/2} = e^{-\lambda t_{1/2}}$ or $\frac{N_t}{N_o} = e^{-\lambda t_{1/2}}$

$$\text{or } ln_{1/2} = -\lambda t_{1/2}$$

$$\text{or, } t_{1/2} = \frac{2{\cdot}303 \log 2}{\lambda} \text{ or } t_{1/2} = \frac{0.693}{\lambda}$$

Half-life of a radio-element is thus independent of its total mass. The half-life of radium (216) is 1590 years, that of radon (222) is 3.8 days and that of polonium (218) is 3 minutes. Half-lives of different radioisotopes actually vary from small fractions of a second to billions of years. Thus in the uranium series the half-life of U^{238} is 4.5×10^9 years and that of Po^{212} is 3×10^{-7} seconds only.

Half-life of a radioelement implies that if we have 400 g. of the radio-element having half-life, say one day, then 200 g. of it will be left after one day, 100 g. at the end of two days, 50 g. at the end of 3 days, 25 g. at the end of 4 days and so on.

Average Life of Radio-elements.

It is to be noted that radio-active disintegration follows an exponential law which implies a definite probability for any particular atom disintegrating at a given moment to be proportional to the total number of atoms present at that moment. The life of any radio-element, that is, the length of time it can exist before it disintegrates can thus have all possible values from zero to infinity. This explains the gradual decay of a radio-element, for otherwise all the atoms would decay at the same time. Hence an average life or mean life for an aggregate of a large number of atoms of radio-element is taken into account.

The average life of a radio-element is the reciprocal of the disintegration constant. Thus, if T_a is the average life, we have, $T_a = \frac{1}{\lambda}$.

Detection and measurement of radioactivity and half-life: Various techniques, such as electroscope, photography, electrometer, ionization chamber etc. had been used to study radioactivity earlier. But recently the measurement of activity and determination of half-life are carried out by sophisticated electronic devices. Geiger-Muller counter, proportional counter, scintillation counter and coincidence counter are some of these modern devices. The ionization produced by a radio-element is multiplied by various techniques and measured under high voltages. The extent of ionization is proportional to the activity of radio-element.

The Geiger-Muller counter consists of a tube shown in Fig. 26—1. The radiations from a radioisotope emitting α, β or γ-rays enter the tube through a thin window. The G—M tube is filled with argon gas under low pressure. The

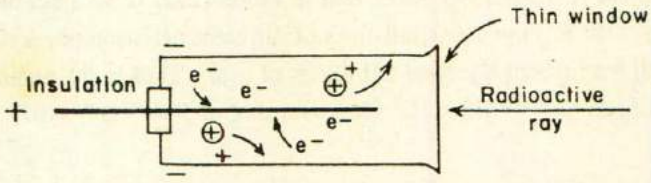


Fig. 26—1. Outline of Geiger-Muller tube for counting radioactive rays.

radioactive rays knock electrons off the argon atoms and form positive argon ions. Under a high external potential of 1000—1200 volts an avalanche of electrons is produced by successive collision and a pulse of electric current flows through the circuit. The continuous discharge is stopped by quenching agents, such as ethyl alcohol or halogen in the tube. The pulse is amplified to operate a microphone or an automatic electronic counter.

Wilson Cloud Chamber enables the path of ionizing radiation from a radioactive element to be seen and photographed. Air saturated with water vapour in a chamber on sudden expansion and cooling provides the medium to follow the track of the radioactive rays. Water vapour is condensed as droplets on the ions formed in the path.

Radioactive rays causes scintillation in some materials such as zinc sulphide or thalium activated sodium iodide crystals which gives out flashes of light on the impact of each radioactive particle or ray. The window of a photo-electric

tube is coated with such a substance and the flash of light causes a pulse of electric current which is amplified and made to operate counting devices.

Thus the radioactivity can be measured in counts per minute or count per second as the case may be.

The activity is proportional to the number of atoms or the quantity of radioisotope. When the radioactivity in terms of, say counts per minute, is plotted against time, the curve obtained is as given in Fig 26—2, which shows the decay curve of a radio-element. But in practice log activity (i. e., log counts per minute) is plotted against time, and a straight line is obtained in the case of a pure radioactive isotope as given in Fig. 26—3. This curve can be used directly to find out the half-life of a radio-element. From the graph in Fig. 26—3, it is found that the time required for the activity to become half the original value is 10 minutes (1000 counts per minute becomes 500 counts per minute in 10 minutes).

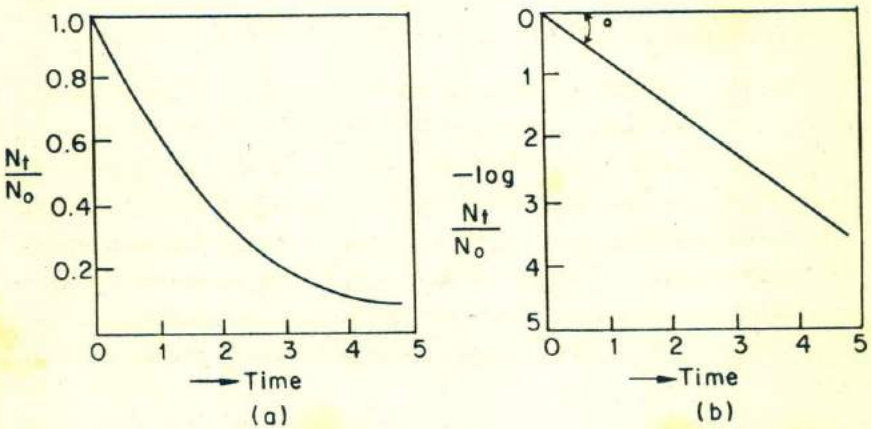


Fig. 26—2. Plot of decay against time. The asymptote curve shows that decay of radio-element follows an exponential law. The log scale gives straight line.

Unit of radioactivity : A *Curie* is the unit of radioactivity and is used in most practical measurements. A *curie* is defined as the quantity of any radioisotope which is undergoing 3.7×10^{10} disintegrations per second. A *Becquerel* is the quantity of a radioisotope undergoing 1 disintegration per second.

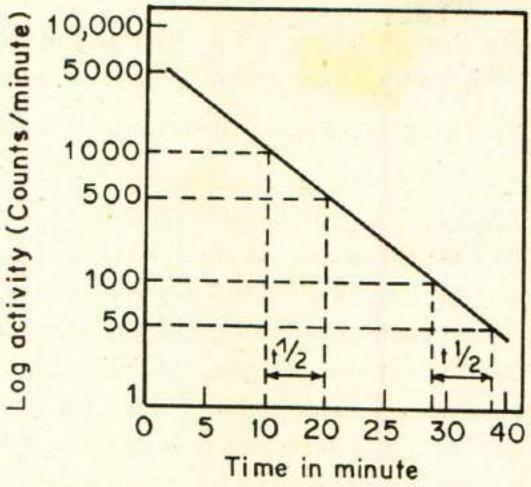


Fig. 26—3. Plot of log activity against time giving a straight line for a pure radio-element. Half-life can be directly read from the graph. $t_{1/2}$ in this case is 10 minutes as indicated.

Nuclear Reactions

It has already been described before that α-particles and electron beams were being used by scientists to investigate the structure of matter. The scattering experiments of Rutherford had already been known, as a result, the existence of a nucleus in an atom was established. Naturally this can be generalized to conclude that if a positively charged particle, such as α-particle, proton or deutron moving with a high velocity, approaches a positively charged nucleus at rest, it tends to be deflected away because of repulsion of the positive charges on each. But if high-energy particle is used it may collide with the nucleus to produce two types of effects :

(1) The high-energy particle is at first absorbed by the nucleus forming a compound nucleus which may be unstable and break up to give a new nucleus and another particle.

(2) The high-energy particle may be absorbed by the nucleus which does not break up but gives out γ-rays.

A nuclear reaction is a process in which a nucleus reacts with another nucleus generally an elementary particle or a photon to produce one or more

nuclei. The high-energy particles used for bombardment in nuclear reactions are known as *projectiles*. The elements subjected to nuclear reactions by projectiles are known as *targets*.

In 1919, Rutherford and his co workers carried out the first nuclear reaction in the laboratory. Using high velocity γ-particles emanating from a radium isotope, Rutherford bombarded nitrogen atoms in a device outlined in Fig. 26—4.

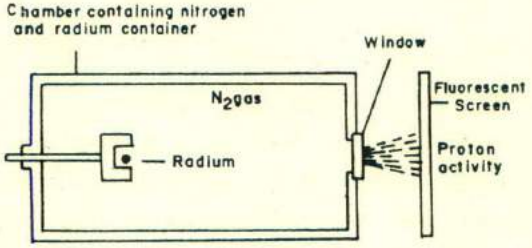


Fig. 26—4. Rutherford apparatus for transmutation of N to O indicated by proton activity on the fluorescent screen.

It was noticed that proton rays were produced when α-particle passed through nitrogen oxygen isotope ${}_8O^{17}$ was formed. ${}_8O^{17}$ is stable and no further change occured. The nuclear reaction is expressed as :

$$ {}_7N^{14} + {}_2He^4 = {}_8O^{17} + {}_1H^1 $$

Notice that the sum of the atomic numbers 9 and the sum of the mass numbers 18, are the same, before and after the nuclear reaction. This reaction is conveniently abbreviated as,

$$ N^{14}(\alpha, p)\, O^{17} $$

which means "α-particle in" and "proton out" in a nuclear reaction involving nitrogen which is converted to oxygen isotope. This reaction was the first "artificial transmutation" as contrasted to "spontaneous transmutation" of elements in nature.

Interest in nuclear structure and the results of high-energy bombardments with projectiles led to the discovery of positron which is a particle similar to electron but with charge+1, by Anderson in 1932. This is designated as e^+, $_{+1}e^0$

or β^+. In the same year Chadwick discovered neutron, a neutral particle having nearly the same mass as proton by carrying out nuclear reaction :

$$_4Be^9 + _2He^4 = _6C^{12} + _0n^1$$

or, $Be^9 (\alpha, n) C^{12}$

Energetics of Nuclear Reactions

Consider the nuclear reaction : $N^{14} (\alpha, p) O^{17}$

The sum of N^{14} + He^4 masses = 18.01141 mass units. The masses of O^{17} + H^1 = 18.01262 mass units. The difference of the mass units is 0.00121. An amount of energy equivalent to 0.00121 mass unit has to be supplied to make the reaction energetically feasible. Since 1 mass unit is equivalent to 931 MeV according to the Einstein's equation $E = mc^2$, the amount of energy 0.00121 x 931 = 1.13 MeV is required to carry out this nuclear reaction.

But it is not possible to carry out the reaction $N^{14} (\alpha , p) O^{17}$ by using α-particle having kinetic energy of 1.13 MeV. The collision between α-particle and N^{17} nucleus is subjected to the conservation of momentum for which 4/18 of kinetic energy of α-particle must be retained by the products. Thus only 14/18 of kinetic energy of α-particle is used for the reaction. But the kinetic energy of the α-particle just capable for carrying out the reaction $N^{14} (\alpha, p) O^{17}$ reaction must be = 18/14 x 1.13 = 1.45 MeV. However, the fraction of the kinetic energy of the projectile retained as the kinetic energy of the products becomes smaller with increasing mass of the target nucleus.

When the mass of the reacting nuclei are not known and if the product nucleus is radioactive disintegrating to the initial nucleus with known decay energy, it is possible to calculate the energy of a nuclear reaction. Thus the reaction

$$_{46}Pd^{106} + _0n^1 \rightarrow _{45}Rh^{106} + p + E$$

$$\downarrow$$

$$_{46}Pd^{106} + \beta^- + 3.55 \text{ MeV}$$

The overall effect in the above reaction is the transformation of neutron into a proton and an electron.

Thus the energy of the nuclear reaction

E = (1.00893 – 1.00812) x 931 – 3.55 MeV = 2.80 MeV will be necessary.

Potential Barrier in Nuclear Reaction

Considering the nuclear reaction, ${}_7N^{14}$ (α, p) ${}_8O^{17}$ it is evident that the coulomb repulsion between the positively charged particles and the nitrogen nucleus creates the potential barrier for the nuclear reaction.

If the charge of the projectile is $Z_1.e$ and the charge of the target nucleus = $Z_2.e$, and if R_1 is the radius of the projectile particle and R_2 the radius of the target nucleus, the coulomb energy to bring these two particles in contact with each other.

$$V = \frac{Z_1, Z_2 \cdot e^2}{R_1 + R_2}$$

The energy of the α-particle must be greater than 3.4 MeV. Rutherford actually used α-particles of over 7 MeV to carry out the reaction. However, the probability of a lower energy particle of "tunnelling through the barrier" exists in accordance with the concept of quantum mechanical approach.

It is therefore visualized that in general it is much easier for neutrons to enter and leave nuclei as compared to the charged particles. Therefore, neutrons of very low energy are most conveniently used for carrying out the nuclear reactions. It is possible to control the energy of neutron to the desired level since neutrons have no charge.

Comparison between Nuclear and Chemical Reactions

1. Both the nuclear and chemical reactions are associated with the absorption and release of energy. In the chemical reaction the valence electrons only participate in the reactions, whereas nucleus are involved nuclear reactions.

2. The quantities of energy in the two types of reactions are vastly of different magnitude.

   In chemical reactions the energy is expressed in terms of cal/mol or Kcal/mole or KJ/mole. But in the case of nuclear reactions it is generally expressed in terms of MeV.

3. Chemical reactions deals with macroscopic amounts of materials in the reactions.

4. Nuclear reactions are very rare and can be brought about by special equipment. Whereas chemical reactions is of common occurrence in nature and carried out for particular purposes which can be easily manipulated.

Nuclear Cross Section

The probability of a nuclear reaction is generally expressed in terms of "Cross Section" represented by σ. The cross section has the dimension of area. The reaction between a nucleus by a projectile which should be uncharged are mainly considered since charged projectiles has to overcome the potential barrier due to coulombic forces. The cross section for a nuclear reaction is expressed by the equation.

$$\sigma = \frac{N}{I.n.x}$$

σ = Cross section for the nuclear reaction expressed in Cm^2 (unit is barn = 10^{-24} Cm^2)

N = Nature and number of nuclear reactions occurring in the target

I = Number of projectiles incident on the target nucleus

n = Number of target nuclei per Cm^3 of the target

x = Thickness of the target in Cm.

The thickness of the target material is an important factor which determines the nuclear cross section i. e. the probability of the nuclear reaction using neutron as the projectile. In most cases the reactions considered are (n, n), (n, γ), (n, p) and (n, α) reactions.

The number N of target nuclei is calculated from the relationship

$$N = \frac{\text{density of the target}}{\text{At, Wt, of the target}} \times 6{,}023 \times 10^{23}$$

Thus in the case of Au^{197} (n, γ) Au^{198} reaction if x = 0.3 Cm and 5 Cm^2 is the area exposed to thermal neutron flux of 10^7 per Cm^2 per sec., the capture cross section of Au^{197} is 95 barns.

Artificial Radioactivity

The first *artificial radioactivity* as distinguished from the natural radioactivity of uranium, thorium and actinium series was discovered by Joliot-Curie in 1934. High energy α-particle was used to bombard aluminium foils as a target. It was found that positrons were emitted and positron activity continued even after stopping the bombardment. The positron activity decreased according to the same disintegration law as the natural radioactivity. When the aluminium target was dissolved in dilute HCl, along with hydrogen PH_3 was also evolved and the solution on oxidation gave a precipitate of an insoluble phosphate. Both the evolution of PH_3 and the phosphate precipitate carried the radioactivity as an isotope of the phosphours :

$$_{13}Al^{27} + {}_2He^4 \rightarrow {}_{15}P^{30} + {}_0n^1$$

$$\downarrow t_{1/2} = 2.5 \text{ minutes}$$

$$_{14}Si^{30} + e^+ \text{ (positron)}$$

Similarly, a boron target when bombarded with α-particle and dissolved in NaOH produced NH_3 gas which was radioactive due to the nuclear reaction forming radioactive isotope of nitrogen:

$$_5B^{10} + {}_2H^4 \rightarrow {}_7N^{13} + {}_0n^1$$

$$\downarrow \text{decays } t_{1/2} = 9.9 \text{ minutes}$$

$$_6C^{13} + e^+$$

These experiments proved the existence of positrons. Other projectiles, other than α-particles such as protons, deutrons and neutrons also produced artificially induced radioactivity. In some cases electrons are produced :

(1) $_{13}Al^{27} + {}_0n^1 \rightarrow {}_{11}Na^{24} + {}_2He^4$,

$_{11}Na^{24} \rightarrow {}_{12}Mg^{24} + {}_{-1}e^\circ$

(2) $_{15}P^{31} + {}_1H^2 \rightarrow {}_{15}P^{32} + {}_1H^1$

$_{15}P^{32} \rightarrow {}_{16}S^{32} + {}_{-1}e^\circ$

(3) $_{28}Ni^{58} + {}_1H^1 \rightarrow {}_{29}Cu^{58} + {}_0n^1$

$_{29}Cu^{58} \rightarrow {}_{28}Ni^8 + {}_{+1}e^\circ$

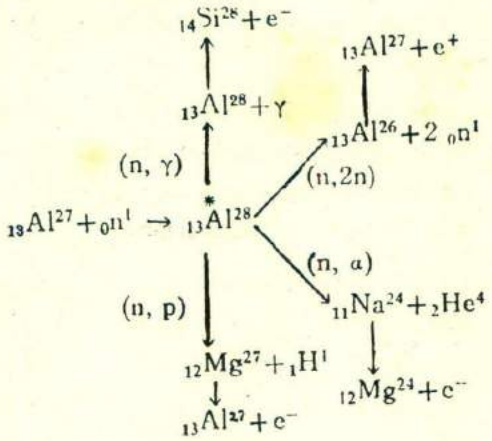
In nuclear reactions when radioactive products are formed by bombardment with high-energy particles, the process is generally known as *artificial radioactivity.*

α-particle is not the only projectile but a number of particles including atomic particles have been used as projectiles. Neutron, n, proton, p, deutron, d, (hydrogen nucleus with mass of 2), are the most common projectiles in nuclear reactions.

It may be noted that neutron being an electrically neutral particle is obviously more advantageous because it can penetrate into the nucleus of an atom easily. But very fast neutrons may just pass through the nucleus without any nuclear reaction. Hence neutrons of controlled energy are generally used to carry out nuclear reactions and depending upon the energy of the neutron projectile a number of different types of processes take place. Thus an aluminium target penetrated by a neutron forms a compound nucleus $_{13}Al^{28}$ which breaks off in a number of ways depending largely on its energy :

Nuclear Fission : A major discovery in nuclear reactions was made in 1936 by Otto Hahn and Strassman in Germany and Fermi in Italy who found that when uranium is used as a target for bombardment with thermal ("slow") neutrons, the uranium nucleus splits into two fragments. Such a process is called *nuclear fission:*

$$_{92}U^{235} + {}_0n^1 \rightarrow {}_{56}Ba^{141} + {}_{36}Kr^{92} + 2\text{–}3\ {}_0n^1 + \text{energy}$$



It is now known that uranium 235 undergoes fission in several different ways:

$$_{92}U^{235} + {}_0n^1 \rightarrow {}_{38}Sr^{93} + {}_{54}Xe^{111} + 2\ {}_0n^1$$

$$_{92}U^{235} + {}_0n^1 \rightarrow {}_{37}Rb^{r89} + {}_{55}Cs^{144} + 3\ {}_0n^1$$

The products on the right hand side of the equation are known as *fission products*. Not only U^{235} but also Pu^{239} undergoes fission with slow neutrons. Th^{232} and U^{238} undergo fission when bombarded with high velocity neutrons.

In this type of reaction a loss of mass occurs which corresponds to the release of a fantastic quantity of energy in accordance with the equation $E = mc^2$. Weight for weight, uranium 235 will produce 2.5 million times energy than coal. On calculation energy released for such reaction are of the order of 200 MeV. Temperature rise is to the order of 10^7°C and the blast of visible, uv, x-ray, γ–rays radiation occur.

Nuclear Reactors : Neutrons are also among the fission products of nuclear reactions and thus it is possible to build an apparatus in which a self-sustaining nuclear chain reaction could occur. The apparatus is generally known as an *atomic reactor* or *pile* or *nuclear reactor*. The number of neutron build-up in the apparatus may take place so rapidly that the chain reaction may lead to the

explosive stage. The chain propagation can be controlled by means of substances called *moderators* such as graphite, heavy water or water which slow down the speed of neutrons and *neutron absorbers*, such as boron or cadmium rods which absorb neutrons.

Pu^{239} is produced in the nuclear reactor by bombarding uranium rods with neutrons. It is uranium 238 which undergoes transmutation (see transuranium elements). Large quantity of cooling water is necessary to cool the reactor. Pu^{239} is separated from the uranium rods by chemical means.

Nuclear reactors are essentially sources of neutrons under controlled conditions. All types of atoms can be used for making both stable and radioactive isotopes, such as cobalt 60, phosphorus 32, sodium 24, carbon 14 etc.

Atomic Energy : The heat energy generated during the fission reaction in an atomic reactor may also be used to raise high pressure steam for turbines and to run dynamos for power production. The technological development of the use of atomic energy will undoubtedly make nuclear fission a prime source of energy in the near future. It is the heat energy which is produced during the nuclear reactions and is used to raise steam under pressure.

Transuranium Elements

A remarkable advancement in science was possible due to the nuclear reaction. Prior to 1940 uranium was the last element having atomic number 92. in 1940 McMillan and Abelson were able to make element 93, neptunium (Np), by bombarding uranium with high velocity deutrons i. e., with (d, p) reaction, Thus,

$$_{92}U^{238} + {}_{1}H^{2} \rightarrow {}_{92}U^{239} + {}_{1}H^{1}$$

$$\downarrow \text{ radioactive}$$

$$_{-1}e^{0} + {}_{94}Pu^{239} \leftarrow {}_{93}Np^{239} + {}_{-1}e^{0}$$

radioactive

The elements, such as neptunium, Np, and plutonium, Pu, which were made artificially and which occur after uranium in the Periodic Table, are called

transuranium elements. Seaborg and his coworkers made a number of transuranium elements by new types of nuclear reactions. Thus:

$$_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{239} \rightarrow {}_{93}Np^{239} + {}_{-1}e^{0}$$

$$\downarrow \beta$$

$$_{92}U^{235} \xleftarrow{\alpha} {}_{94}Pu^{239}$$

$$_{94}Pu^{239} + {}_{2}He^{4} \rightarrow {}_{96}Cm^{242} + {}_{0}n^{1}$$

$$_{96}Cm^{242} + {}_{2}He^{4} \rightarrow {}_{98}Cf^{244} + 2\ {}_{0}n^{1}$$

The higher transuranium elements upto atomic number 105 have been made by various other nuclear reactions including the use of atomic particles as projectiles. These bombardment reactions, using such reactors as Van de Graff generators, *Cyclotron, Synchrotron, Betatron, Linear accelerators* etc. Fig. 26—5 gives an schematic diagram of a cyclotron generally used to accelerate protons and deutrons. The Van de Graff generators is used to build up huge voltage differences. The betatron is employed for obtaining high velocity electrons. The synchrotron and liner accelerator are used to produce charged particles of extremely high energies. In the cyclotron, as illustrated in Fig. 26—5, the ions produced at the source in the centre are accelerated between the "*dees*". Each "*dee*' between a high magnetic field becomes alternately charged positively, then negatively about 12 million times per second. The particles become greatly accelerated and after attaining very high energy (velocity), they leave the "*dee*" and strike the target to produce the desired nuclear reactions.

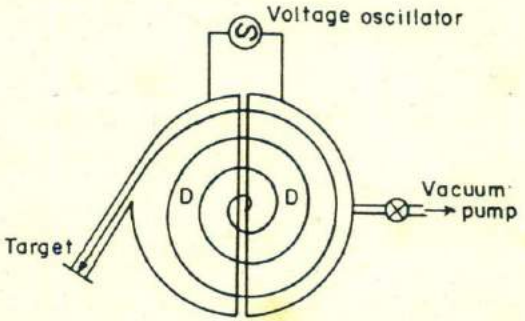


Fig. 26—5. Schematic diagram of a cyclotron for acceleration of charged particles.

The Atomic Bomb : Although the theoretical aspects of the production of atomic bomb using uranium 235 and plutonium 239 involving nuclear fission and large energy evolution by the chain reaction appear to be simple, the technology is highly complex. In this connection the *critical mass* of the fissionable material is a necessary factor. Samples of uranium 235, less massive than the critical mass, will not explode. But a terrific explosion occurs if two or more pieces of U—235 or Pu—239 having a total mass equal to the critical mass are brought in contact with each other. A stray cosmic ray neutron is all that is necessary to trigger this nuclear chain reaction.

Nuclear Fusion (The Hydrogen Bomb) : Nuclear fusion involves reaction between two or more nuclei to produce new nuclei. Nuclear fusion involving the isotopes of hydrogen are specially exothermic because the packing fraction of a hydrogen nuclide is larger than that of any other nuclide. Examples of nuclear fusion reactions for use in hydrogen (thermonuclear) bombs are:

$$_1H^2 + {}_1H^3 \rightarrow {}_2He^4 + {}_0n^1$$

$$_1H^3 + {}_1H^3 \rightarrow {}_2He^4 + 2\,{}_0n^1$$

$$_3Li^7 + {}_1H^2 \rightarrow 2\,{}_2He^4 + {}_0n^1$$

These reactions require very high energy to get started since they involve interaction between nuclides of like charges and comparable masses. The technology of hydrogen bomb is different from the nuclear fission bomb. There is no critical mass and no neutron is required to trigger the reaction. However, the high energy required may be derived from the nuclear fission for bringing about the nuclear fusion.

It is believed that solar energy is due to a series of nuclear fusion reactions taking place in the sun ultimately leading to the step-wise transformation from protium ($_1H^1$) atoms to one He :

$$4\,{}_1H^1 \rightarrow {}_2He^4 + 2e^+ + \gamma$$

The two positrons encounter two electrons and all the four particles are annihilated releasing tremendous amount of energy.

Radioisotopes

There are about 280 stable naturally occurring isotopes, 73 natural radioisotopes and in addition about 1000 or more artificial radioisotopes which have been made and identified. All the isotopes of elements beyond bismuth, atomic number 93, are naturally radioactive.

Constitution of isotopes : Isotopes are elements occupying the same place in the Periodic Table which is based upon the atomic number of elements. Isotopes are, therefore, elements having the same atomic number but different mass numbers. The atomic number is the number of positive charges, i. e., the number of protons in the nucleus of the atom. It is also the number of extra-nuclear electrons in a neutral atom. The nucleus of an element, for all practical purposes, may be supposed to consist entirely of protons and neutrons. These together make up almost the entire mass of the atom.

An element must have fixed number of protons ; but the number of neutrons varies so that it is possible to have several kinds of nuclei of different weights. For instance, atoms having 6 protons exist in 5 different weights.

Carbon—10	6 protons	+	4 neutrons	
C—11	6 "	+	5	
C—12	6 "	+	6	"
C—13	6 "	+	7	"
C—14	6 "	+	8	"

Similarly, oxygen may have the following isotopes:

Oxygen —16	8 protons	+	8 neutrons	
O—17	8 "	+	9	"
O—18	8 "	+	10	"

There are two important questions which arise :

(1) Why so many protons could be packed together within a nucleus ? The protons are expected to fly off from each other due to repulsion of positive charges.

(2) Why some isotopes are stable, whereas a large number of them are radioactive and undergo disintegration ? Stable isotopes are those which do not emit any detectable radiations.

The answer to these questions are given in the considerations of nuclear stability.

Nuclear Structure and Nuclear Stability

Nuclear structure : The nuclei of elements, for all practical purposes, consist of protons and neutrons except the hydrogen nucleus which contains only one proton. Neutrons and protons together are called *nucleons*.

The protons and neutrons within a nucleus are held together by means of forces known as *Nuclear Forces*. Nuclear forces are at least millions of times greater than those which bind atoms in a molecule. These forces operate only at very close range and hence nuclear forces are short-range forces and the packing of the nuclear particles are so close that the density is 130 million tons/c.c. The radius of the nucleus varies from about 2×10^{-13} cm. for He to about 8×10^{-13} cm. for U.

The nuclear forces are quite different from the electrostatic and gravitational forces and in a nucleus they arise due to interaction between the proton and neutron. These are designated as :

proton—proton interaction	(p—p)
neutron—neutron interaction	(n—n)
proton—neutron interaction	(p—n)

When the number of protons is high as in the case of elements of higher atomic number, there is a sharp increase in the number of neutrons to hold the nucleus together. It is, therefore, assumed that neutrons must be at least partly responsible for the binding of nucleus. Thus the neutrons provide a sort of *"nuclear glue"* for the nucleus.

A number of theories have been advanced to explain the structure of the nucleus. It has been assumed that protons and neutrons are arranged in *nuclear energy levels* just as the electrons. It is also believed that the nuclear particles are held together by π-mesons. During the conversion of a proton to neutron or a

neutron to proton, π- mesons are produced and absorbed, and a nuclear particle called neutrino (ν) with almost zero mass and charge is released as a result of the exchange phenomenon. This question still remains essentially unanswered.

The liquid drop model of nucleus proposed by Bohr imagines the nucleus as consisting of neutrons and protons in a random manner like the molecules in a drop of liquid. This idea is supported by almost the same nuclear density of all the elements. The nuclear-shell model considers nuclear particles arranged in a systematic manner in different energy levels like the electrons. This is supported by the fact that Pauli Exclusion Principle is applicable on nuclear particles which have spin and momentum. Thus nuclei containing even number of nucleons of either kind are stable and plentiful and nuclei having the proton or neutron equal to the so-called *magic numbers*, 2, 8, 20, 28, 50, 82 and 126 are stable.

Nuclear Binding Energy

The nuclear binding energy is the energy released when two or more nuclear particles form a nucleus. Conversely, this is also the theoretical measure of the energy required to disrupt a nucleus into constituent parts.

The difference between the masses of the nucleus and the sum of the individual mass of the component parts (neutrons and protons) provide a measure of the energy that is liberated when the nucleus is built from its components.

Mass of each isotope is a whole number known as the *Mass Number*. The exact value of the mass of an atom in called the *atomic mass* .

In view of the fact that isotopic masses are whole numbers, they can not be exact multiples of the masses of neutron (1.00893) and proton (1.00758). For example, the helium nucleus contains 2 neutrons and 2 protons. The mass of helium nucleus is:

$$(2 \times 1.00759) + (2 \times 1.00897) = 4.03312$$

But the actual mass of helium nucleus is 4.00277. The difference between the expected mass and the actual mass is $4.03312 - 4.00277 = 0.03035$ mass unit. This difference between the actual mass of an atom and that expected from the mass of its components (neutrons and protons) is known as *Mass Defect*.

Thus, in the formation of a helium nucleus with two neutrons and two protons there is actually a loss of mass (0.03035 units). This mass defect principle is true for all the nuclei.

Mass-Energy Relationship

The loss of mass during the formation of an atom from its components is explained on the basis of Einstein's theory that such reactions involve change of mass into energy according to the equation, $E = mc^2$, where E is the energy, m stands for mass and c is the velocity of light. According to this equation it can be calculated that 1 g. of matter can liberate 2.15×10^{13} calories, or 9×10^{20} ergs or 931 million electron volts (MeV) of energy. Thus one atomic mass unit (a.m.u) is equivalent to 931MeV of energy. In the case of the formation of He nucleus by using 2 protons and 2 neutrons the mass defect is equal to 0.0304 a. m. u. This is equivalent to 6.5×10^{11} calories of heat or about 28 MeV of energy. (1 MeV = 1.6×10^{-6} erg).

Thus the breakdown or the formation of a stable nucleus from its component parts involves a very large amount of energy. The decrease in mass from that of the neutrons and the protons from which the nucleus may be considered to be formed is called the *Packing Effect*. The greater the loss of mass (Packing Effect), the more stable the nucleus. Thus the mass defect is actually a measure of the nuclear binding energy.

Neutron-Proton Ratio

Stability of atomic nuclei : The stability of the nucleus of an atom is related to the ratio of the number of neutrons to the number of protons in the nucleus. For lighter elements upto atomic slumber 20, the neutron to proton ratio (n/p) is close to 1. For stable isotopes of elements of higher atomic numbers the n/p ratio increases until it reaches 1.52 for bismuth ($_{83}Bi^{200}$). After bismuth the excessive number of neutrons imparts instability to the nuclei which occur in nature. Hence all isotopes with atomic number greater than 83 are radioactive. For each stable nucleus there is an optimum range of n/p within which the isotopes of that nucleus will be stable. It is observed from the curve in Fig. 26—6 that the straight line corresponds to n/p ratio of those nuclei which would have equal number of neutrons and protons (n = p). The light

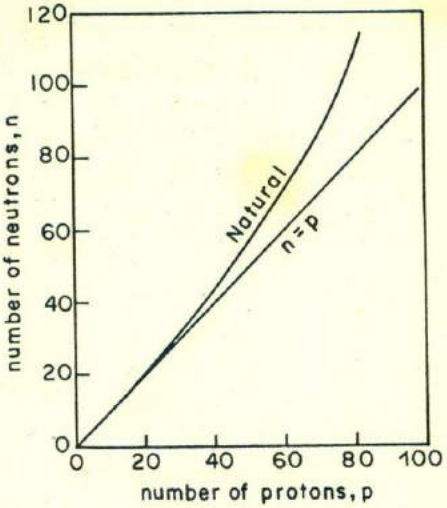


Fig 26—6. Neutron-proton ratio in nuclei of element.

non-radioactive elements contain almost equal number of neutrons and protons as is seen from the lower portion of the curved line in the Fig. 26—6 which also shows that stable nuclei of heavier elements require more neutrons for stability.

Those nuclei having n/p ratios outside the natural stability curve are generally radioactive. In such cases, the n/p ratio is either too high or too low for stability and these have tendency to decay in order to adjust n/p ratio to more stable one by several ways :—

(i) The isotopes having too many neutrons will disintegrate by α- or β–emission. β-particles are formed within the nucleus due to the conversion of a neutron to proton :

$$n \rightarrow p + \beta$$

Thus $$_6C^{14} \rightarrow {}_7N^{14} + \beta$$

(ii) Alternatively the nucleus may capture an orbital electron (K-capture) to readjust excess proton which is converted to neutron by this process. This capture is always accompanied by emission of X-rays or γ-rays.

$$p + e \rightarrow n$$

Thus $$_{80}Hg^{197} + e \rightarrow {}_{79}Au^{197}$$

(iii) Decrease of positive charge on the nucleus may also be achieved by positron emission. This is observed in artificial radio isotopes only.

$$p + n \rightarrow e^+$$

Thus $$_{15}P^{30} \rightarrow {}_{14}Si^{30} + e^+$$

(iv) α-decay : (2p + 2n out from nucleus) = $_2He^4$

Thus $$_{84}Po^{210} \rightarrow {}_{82}Pb^{206} + {}_2He^4$$

(v) γ-radiation : γ-rays are emitted due to energy changes within the nucleus when an excited nucleus drops down to a lower nuclear energy level. This is frequently accompanied during α, β or β^+ emission :

$$^*_{92}U^{236} \text{ (excited state)} \rightarrow \gamma$$

(vi) Neutron emission. Thus : $_2He^5 \rightarrow {}_2He^4 + {}_0n^1$

Isobars :Most elements have two or more isotopes. But we also come across with the nuclei of different elements which have the same mass number. Different elements that have the same mass numbers but different atomic numbers are called *Isobars*. The total number of neutrons and protons is the same but the number of protons is different. Thus the following elements are isobar pairs :

Cr	24p + 30n =	54 mass number
Fe	26p + 28n =	54 mass number
Cd	48p + 68n =	116 mass number
Sn	50p + 66n =	116 mass number

Methods of Separation of Isotopes

Separation of isotopes : By definition it can be seen that the isotopes of an element vary in mass but not in chemical properties. The only method which may be applied to isotopic separation depends on properties related to mass. It may be mentioned that separation of isotopes has now assumed a great importance from the practical point of view in the field of atomic energy where large quantities of fissionable materials, such as U^{235}, are required.

There are a number of methods for the separation of isotopes and only three methods are described.

The separation of isotopes depends mostly on physical properties related to mass. Thus in a gas composed of two isotopes of an element the average kinetic energy of the lighter isotope molecules and that of the heavier isotope molecules are the same. Therefore, the speed of the lighter molecules must be greater than that of the heavier molecules. Thus under the influence of external forces the lighter and heavier molecules can be made to move with different speed.

Similarly, isotopes of the same element may differ appreciably in their reactivities particularly in the case of lighter elements, such as H^1 and H^2. This gives rise to variation in reaction rates of isotopic molecules. Based on this principle, chemical methods have also been devised for the separation of isotopes.

The various methods of separation of isotopes may be listed as follows.

1. The gaseous diffusion method ;
2. The electromagnetic method ;
3. The thermal diffusion method ;
4. The distillation method ;
5. The centrifugal method ;
6. The electrolytic method ;
7. The chemical exchange method.

Brief description of three methods are given :—

1. The gaseous-diffusion method : The rates of diffusion of different gases through a porous material are inversely proportional to the square roots of their densities at the same temperature. Thus two gases of different molecules having masses m_1 and m_2 will have velocities v_1 and v_2.The kinetic energies of the two molecules are equal. Therefore,

$$\tfrac{1}{2} m_1 v_1^2 = \tfrac{1}{2} m_2 v_2^2$$

or
$$\frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}}$$

which is Graham's Law of Diffusion.

Based on this principle, uranium isotopes, U^{238} and U^{235}, have been separated from the point of view of the importance of U^{235} which is a nuclear fuel. The compound used is UF_6 in the gaseous state containing $U^{238}F_6$ and $U^{235}F_6$ in the ratio of 99.3% and 0.7% respectively. After separation $U^{235}F_6$ is about 99% pure after passing through approximately 4000 diffusion stages.

2. The electromagnetic method : The principle of the electromagnetic separation of isotope is the same as the mass spectrograph in which isotopes of different masses when passed through a magnetic field separate into light and heavy particles. A sketch of the principle of electromagnetic separation is given in the Fig. 26—7. This method is now-a-days used to separate most of the isotopes throughout the Periodic Table mostly for the purpose of study and research. It is highly costly on commercial lines.

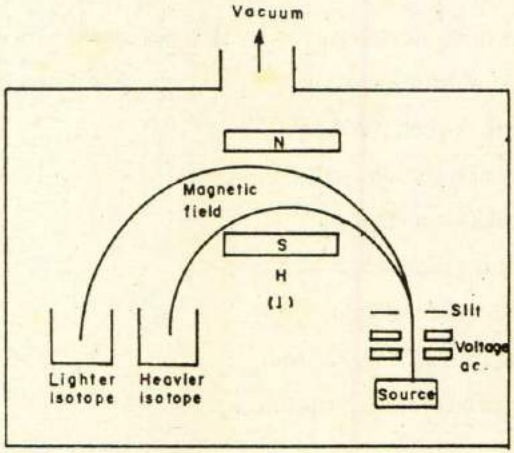


Fig. 26—7. Separation of isotopes by the electromagnetic method.

3. The distillation method : Separation of isotopes on the basis of their vapour pressure has been achieved in the case of mercury, deuterium (D_2O from H_2O) etc. The difference in vapour pressure arises due to different masses. Fig. 26—8 shows the arrangement for separation of mercury isotopes by partial vacuum between the walls of Dewar flask. The lighter isotopes are condensed at the bottom part of the inner flask cooled with liquid air.

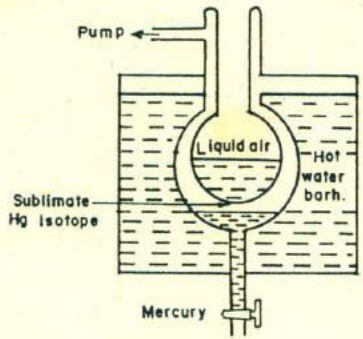


Fig. 26—8. Separation of Hg isotopes by distillation method.

Application of Radioisotopes

The characteristics of radioisotopes as displayed by its half-life and the type of radiation, make it possible for a wide range of utilization in industry, agriculture, biology and space research. The numerous fields where radioisotopes and even stable isotopes have been used are so vast that now-a-days it has given rise to a new branch of chemistry known as *Tracer Chemistry*. We shall focus upon a few instance of isolated fields of applications to illustrate this powerful technique developed in this modern time.

Techniques of applications : A number of techniques, such as isotope dilution and activation methods. have been developed for the application of isotopes. Some of the fields of application are given below as typical examples.

1. Mechanical applications : Radiation gauges have been developed for many industrial applications, such as production of linoleum, steel sheet, coated paper, plastic film, internal diameters of tubes etc. Thickness of a thin film strip of, say, aluminium or paper or plastic speeding through rollers can be measured by means of a radioisotope held below the film so that its radiation goes upward through the moving strip. A radioisotope is chosen for the job so that its radiations are substantially absorbed in the film. On the other side of the film, a detector head, such as a G. M. counter, is mounted to monitor the number of rays passing through the moving strip. The electronic output of the counter is a measure of the film thickness. Variations in counter output corres-

pond to changes in thickness. A signal advantage is that there is no mechanical contact with the moving film. The G. M. counter output can be coupled to drive mechanism of the rolling or coating machine. In this way the rolling or coating process can be subjected to automation to produce a uniform product.

2. Chemical analysis : Detection, identification and quantitative determinations of materials could be easily and advantageously carried out and could be applied where other methods simply fail. Besides analytical problems, both synthetic and reaction mechanism could be studied by using radioisotopes as "tags" to lable chemical compound of extreme complexity in course of chemical reaction. Thus hydrolysis, saponification, rates of reactions and changes in structures of chemical species are advantageously investigated.

3. Radioisotopes in medicine : These are used for both diagnostic and therapeutic purposes. The application generally results from the fact that certain elements are preferentially absorbed by definite types of tissues. Destruction of cancerous tissues by cobalt—60 and natural radium is well-known. Phosphorus—32 has been used to control polycythemiavera, a condition where blood contains too many red corpuscles. The disease is located in the bone marrow. Iodine—131 is used for treatment of certain thyroid complaints. Functions of liver, mucous membrane and other vital organs of body have been studied.

4. Agricultural applications : The transportation of mineral nutrients from roots to leaves and subsequent redistribution within plants can be planned through the use of radioisotopes and radioautography. Improvement of irrigation feed water and fertilizers and their actions on the food crops have been made. Preservations of agricultural farm produce have been achieved, such as sprouting of potatoes has been prevented. Preservation of fish, meat and eggs could be done. Shelf life of perishable fruits and vegetables has been extended.

5. Industrial applications : The field of industrial applications of radioisotopes are varied and numerous. Measuring levels of liquid in closed tanks by floats containing radioisotopes, thickness of sheets, counting of tablets, pills and cigarettes in packets, functions of plasticizers in tyers and tubes, metallurgical operations producing special alloys etc. are some of them. Internal cracks can be located by radioautography. Mixing of ingredients in an industrial

product could be traced. Different grades of petroleum can be transmitted through the same pipe.

6. Measurement of time : Atomic clock which measures time by the actions of an electric current on cesium atom spinning in vacuum has an accuracy of one second in 3000 years. The age of the earth and the age of archaeological samples have been found by radiocarbon dating. The ratio of C^{14}/C^{12} is fixed in the atmosphere because of the continuous production of C^{14} by neutrons present in cosmic rays :

$$_7N^{14} + {}_0n^1 \rightarrow {}_{12}C^{14} + {}_1H^1$$

$C^{14}O_2$ and $C^{12}O_2$ both are taken up by living things and C^{14}/C^{12} ratio is the same as that in the atmosphere. But after death the living things does not absorb CO_2 and the C^{14} in the system begins to lose its activity. The half-life of C^{14} is 5770 years and the activity left in the system gives a measure of the date when it existed or first made. Even freshness of water and other materials can also be determined by the hydrogen istotope Tritium. Internally deposited radioisotopes are used as time markers which establish the date of origin of the product. Very small quantity of harmless radioisotopes are used for this purpose.

7. Biological applications : Tracer method by radioisotopes has been applied extensively in the field of biology and biochemistry and living things. For instance, the various biological and biochemical processes, such as transport of ions across cell membranes, metabolic interconversions, food and mineral metabolism and particularly the dynamics of the steady state in living beings have been explored to gain better understanding of living things. It has now been established that the entire structure of man changes to a new structure within the course of one year. This was possible by using calcium—44, a radioisotope of calcium. The natural phenomenon of photosynthesis has been studied with radioactive carbondioxide and it has been established that phosphoglyceric acid is the first stable compound produced by a plant in photosynthesis.

8. In forensic science : Radioisotopes help in tracking down the activities of counterfeiters who must necessarily draw upon certain commercial sources of ink, paper and other materials. Narcotic rings may be disrupted if their

sources of supply can be identified. An isotopic technique has been developed to trace drug samples back to their place of origin.

9. Isotope for power generation : Discs of strontium titanate are sealed inside a cylinder to isolate the radioactivity due to strontium—90, a hazardous radioisotope. Heat produced by the 17,500 curies of strontium—90 inside the cylinder is converted by means of thermoelectric elements into five watts of power which can run weather station and transmit atomspheric data.

10. Living molecules : Now-a-days extensive studies are being made to unravel the mystery of life and living molecules. Study of renewal rates of phosphatides and carbohydrates and the formation rate of desoxyribonucleic acid and ribonucleic acid (DNA and RNA) using phosphorus—32 and carbon—14 has revealed more mysteries of nature of living organisms and it appears probable that man would be able to create living molecules in future.

QUESTIONS AND PROBLEMS

1. Write notes on the following :—
   (a) Half-life period of radioactive element ;
   (b) Radioactive equilibrium ;
   (c) Artificial radioactivity ;
   (d) Packing fraction ;
   (e) Half-life of a radioisotope ;
   (f) Geiger counter ;
   (g) Uses of radioisotopes.
2. What is radioactivity and how was it discovered? Describe the properties of radiation obtained from radium.
3. What do you understand by Isotopes and Isobars? By what methods can isotopes be identified ? Indicate the importance of isotopes.
4. How are isotopes detected ? Give an account of the basis of the method of separation of isotopes.
5. What are isotopes? How are the isotopes of an element identified ?

6. What is radioactivity ? Describe the properties of the radiation obtained from radium? What information has this knowledge contributed to the mechanism of radioactivity ?

7. Explain the following with illustrations :—

   (a) Half-life of a radioelement ;

   (b) Nuclear reaction.

8. Write a short note on radioactivity.

9. Write short notes on :—

   (a) Isotopes ;

   (b) Uses of radioisotopes ;

   (c) properties of α, β and γ-rays.

10. Answer the following :—

   (a) What are alpha particles? Describe some nuclear reactions that take place by bombardment with alpha particles. What other particles are utilized for nuclear reactions ?

   (b) Explain, with illustrations, the term isotopes. Discuss briefly the principles underlying two methods of separation of isotopes.

11. Write a short note on discovery of radioactivity.

12. (a) How will you detect and measure radioactivity?

   (b) $_{13}Al^{27}$ on bombardment with alpha particles yields $_{15}P^{30}$ which is radioactive and emits a positron. Write the equations for the nuclear reactions involved.

13. What is the difference between natural and artificial radioactivity? Describe three types of artificial disintegration of atoms with suitable examples.

14. Write notes on :—

   (a) Radioactivity, (b) Nuclear Reactions, (c) Heavy hydrogen, (d) Uses of Radioisotopes.

18. Write explanatory note on radioactivity equilibrium and Half-life of radioactivity.

19. The radioactive decay constant of radium is 1.36×10^{-11}. How many discintegradions per second occur in 100 g of radium.

20. How many α-particles per second would be emitted from 4×10^{-12} g of ^{210}Po ($t_{1/2}$ = 138 days)?

21. 2.0 g of 33P decays by β emission to 0.25 g in 75.9 days. Find the ($t_{1/2}$ of 33P.

CHAPTER 27

CHEMISTRY OF SOME RADIOACTIVE ELEMENTS

(Radium. Thorium, Uranium and Plutonium)

The chemistry of radioactive elements, natural or artificial, follows the pattern of the periodic relationship of the group of elements to which they belong. Apart from the special phenomenon of radioactivity, their chemistry is quite ordinary and is concerned almost entirely with the properties which depend upon the valence electrons. The phenomenon of radioactivity is connected with the nuclear structures but the chemistry is concerned with the electron arrangement of the outermost orbitals.

Radium

Radium is the last element of the alkaline earth family, group IIA, as has been mentioned before (page 372). It has almost identical physical and chemical properties with those of barium. In accordance with the gradation of group properties, the following points may be noted :—

(i) Radium is the most reactive metal of group IIA.

(ii) $Ra(OH)_2$ is fairly soluble in water like $Ba(OH)_2$ and the solution gives a strong base.

(iii) $RaSO_4$ is insoluble in acids and ammonia like $BaSO_4$,

(iv) Ra-compounds are isomorphous with the corresponding compounds of Barrium.

Discovery of Radium

With the help of a gold-leaf electroscope, which measures the extent of ionization produced by a radioactive substance, Madam Curie studied the residue

of the uranium ore, *pitchblende* (mostly U_3O_8), after the extraction of uranium. She found that a sample of the residue on concentration was more active than the same weight of a purified uranium salt. This indicated the presence of a more radioactive substance in the ore residue than uranium. In 1898 Madam Curie succeeded in isolating a very active substance in the form of bromide from a large quantity of pitchblende after a long and tedious process of extraction and fractional crystallization. This salt was a million times more active than the same salt of uranium. The salt isolated was radium bromide and thus the discovery of new radioactive element, radium, was announced.

Extraction of Radium

Sources : Pitchblende (mainly U_3O_8)

Carnotite [mainly $K_2[(UO_2)_2(VO_4)_2.8H_2O]$

or $K_2O.\ 2UO_3.\ V_2O_5.\ xH_2O$

The process of extraction depends upon the type of mineral. The precipitation of the insoluble sulphates and subsequent isolation of barium and radium are the main principles involved. A simple flow-sheet for the isolation of $RaCl_2$ is given on page 792.

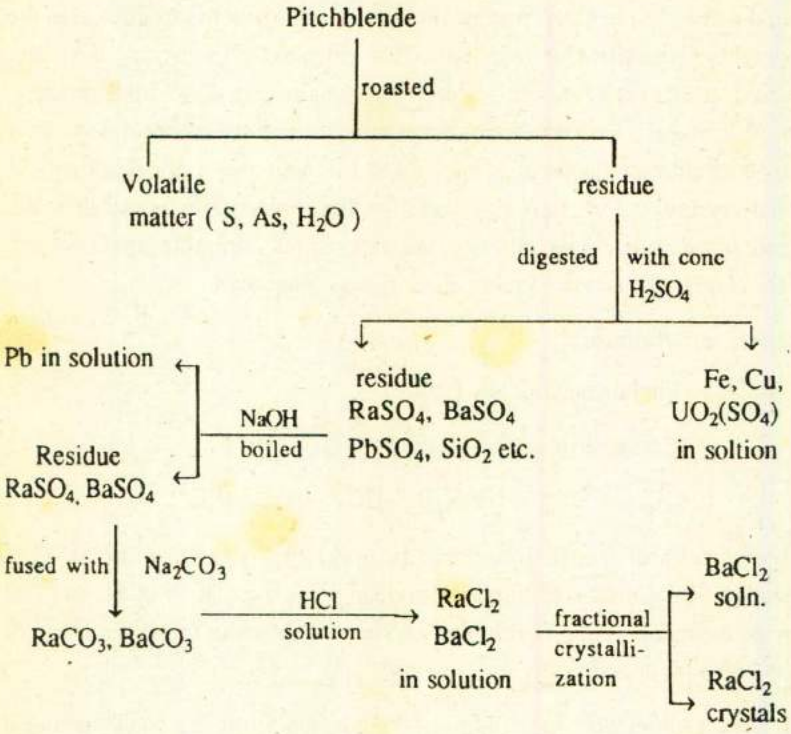
Metallic radium was first obtained by Madam Curie by electrolysing a solution of $RaCl_2$ with a Hg-cathode and platinum-iridium anode. Ra-amalgam obtained is distilled to remove mercury.

Properties of Ra : It is a white metal, rapidly tarnishes in air. It has similar physical and chemical properties as those of barium.

Ra metal reacts with water forming $Ra(OH)_2$ in solution and evolving hydrogen. It dissolves in dilute HCl giving $RaCl_2$. It also absorbs nitrogen forming nitride, Ra_3N_2. It is the most reactive of all the alkaline earth elements.

$RaCl_2.2H_2O$ is isomorphous with $BaCl_2.2H_2O$ but less soluble in water than barium chloride. $RaSO_4$ is less soluble in water than $BaSO_4$. Ra-salts are obtained by the action of acid on $RaCO_3$.

Ra metal and all its compounds in any form are radioactive and disintegrate with half-life of 1590 years into radon $_{88}Ra^{226} \rightarrow _{86}Rn^{222} + He^4 +$ energy. The



products of disintegration are both gases. The gases are obtained when a radium salt such as $RaCl_2$, is dissolved in water and boiled. Radon and helium together with H_2 and O_2 (from the decomposition of H_2O) are evolved. The salts of Ra glow in the dark with green phosphorescence.

Uses : Ra-salts mixed with ZnS, fluorspar etc, are made into luminous paints. Radium is used in the treatment of cancer and malignant tumour.

THE ACTINIDE SERIES

In order to discuss the individual chemistry of thorium,, uranium and plutonium from the modern stand point, it is necessary to mention that these three radioclements are members of a series of elements known as the *Actinide Series* (page 138). This series begins with Actinium, element 89, and extends upto Lawrencium. element 103. The series are analogous to the rare earth

elements known as the *Lanthanides*. The electronic configurations of the Actinide Series are built up in a similar manner as the lanthanides but electrons orbitals involved are 5f or 6d. The outer electron orbitals of some of the actinide elements are represented as follows :

Ac (89)—radon core + $6d^1 7s^2$

Th (90)—radon core + $6d^2 7s^2$

Pa (91)—radon core + $5f^2 6d^1 7s^2$

U (92)—radon core + $5f^3 6d^1 7s^2$

↓

Am (95)—radone core + $5f^7 6d^0 7s^2$

Cm(96)—radon core + $5f^7 6d^1 7s^2$

Bk (97)—radon core + $5f^9 6d^0 7s^2$

↓

Lr(103)—radon core + $5f^{14} 6d^1 7s^2$

Although there are some controversy regarding the electronic configurations but, in general, the chemistry of these elements follows the pattern of rare earths. These elements have characteristic valence of +3, but show much wider variations in oxidation states due to larger sizes of the atomic radii. Thorium resembles cerium in that it has a oxidation state of +4.

From element 93—103 (neptunium to lawrencium) the series is generally called as transuranium elements and are all made by artificial means (see page 774).

Thorium, uranium and plutonium are of great importance in this atomic age because of their use in the development of atomic energy both for war and peace.

Thorium

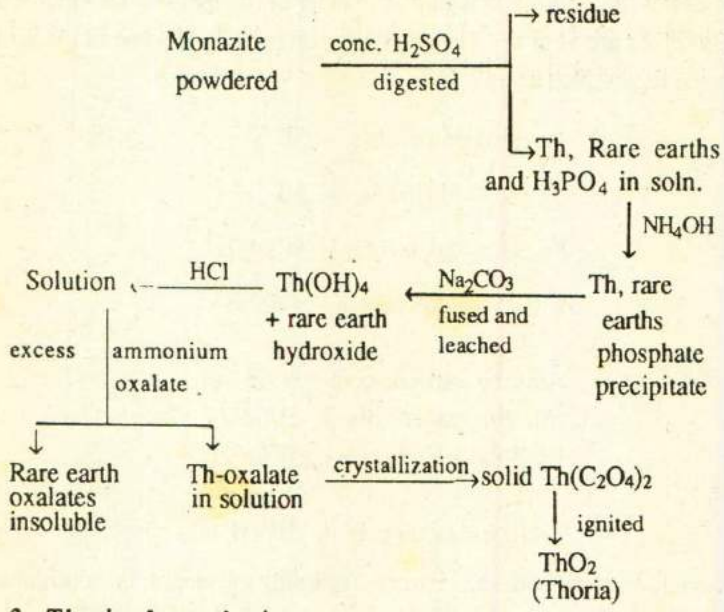
Sources : Thorite—$ThSiO_4$

Monazite—Th, Ce, La etc. as phophate

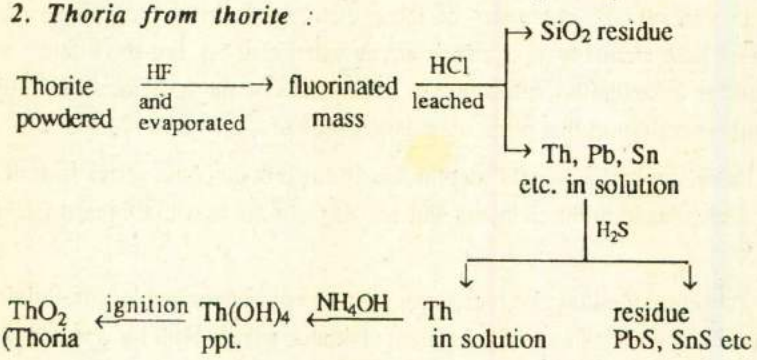
Thorianite—ThO_2+UO_2

Extraction : The following procedures are generally adopted to separate Th from other substances present in the mineral monazite and thorite :

1. Thoria from monazite :



2. Thoria from thorite :



Other compounds of thorium, such as $Th(NO_3)_4$. $Th(SO)_4)_2$, etc. may be obtained by dissolving $Th(OH)_4$ in the appropriate acids and crystallization. $ThCl_4$ is obtained by heating a mixture of ThO_2 and carbon in Cl_2 gas :

$$ThO_2 + 2C + 2Cl_2 = ThCl_4 + 2CO_4$$

Metallic Th is obtained by reducing $ThCl_4$ with Na or K.

Thorium has very similar chemistry as that of the elements of group IVB (Ti, Hf, Zr). It has + 4 as the most common oxidation state. $Th(OH)_4$ is much more basic and Th-salts are not appreciably hydrolysed in water.

Uses : Thoria, ThO_2, mixed with CeO_2, is used in the manufacture of gas mantles. Tungsten filaments in electric lamps are also given a coat of thoria to increase their efficiency. Recently thorium has acquired an strategic importance of its application in the field of atomic energy.

Uranium

Uranium was the first radioactive element to be discovered in pitchblende.

Sources : Pitchblende—(mainly U_3O_8) or (Uraninite)

Carnotite—$K_2(UO_2)_2.(VO_4)_2.8H_2O$

or $K_2O.2UO_3.V_2O_5.xH_2O$

Extraction of uranium : There are several methods for the processing of the uranium mineral and subsequent extraction of the metal which is of great importance in the atomic age as a nuclear fuel. One of the methods is based on the reduction of the mineral pitchblende (U_3O_8) to UO_2 by carbon or natural gas. UO_2 on chlorination with $COCl_2$ or CCl_4 gives UCl_4 which is reduced to metallic uranium by heating with Ca or Ba.

$$\underset{\text{powdered}}{\text{Pitchblende } (U_3O_8)} \xrightarrow[\text{heat}]{CH_4} \underset{UO_2}{\text{Uranous dioxide}} \xrightarrow[\text{or } CCl_4]{COCl_2} \underset{UCl_4}{\text{Uranous tetrachloride}} \xrightarrow[\text{heat}]{+\ \text{Ca or Ba}} \text{Uranium metal}$$

Uranium metal is also obtained by heating UF_4 with Mg or Ca :

$$UF_4 + 2Ca = U + 2CaF_2$$

Properties of uranium : Uranium metal has the appearance of nickel and is white to look at. It melts at 1850°C. It has a high density of about 19

g/cm^3. It occurs in several isotopes of which U^{238} and U^{235} are most abundant in nature.

Uranium is moderately active and reacts with halogens, sulphur, nitrogen and acids etc. It reacts with water slowly in the cold but rapidly on boiling. Alkali solutions have no action on uranium.

Compounds of uranium : Uranium shows oxidation states of +2, +3, +4, +5 and +6 but the most important oxidation states are +4 and +6. The chemistry of uranium follows the same pattern as the elements of group VIB (Cr, Mo, W). The +4 and +6 states are stable in aqueous solutions. UCl_3 and UCl_5 may be formed at high temperature but are unstable in water.

Uranyl compounds : The hexavalent uranium exists in acid solution as UO_2^{+2} (uranyl ion) and many uranium salts, such as $UO_2(NO_3)_2$, $UO_2(OOCCH_3)_2$, UO_2SO_4, UO_2Cl_2 etc. are well-difined compounds. These compounds are also commonly called uranium salts. The processing of mineral U_3O_8 with conc H_2SO_4 and subsequent precipitation of uranium by NH_4OH or $(NH_4)_2CO_3$ give $UO_2(OH)_2$ or UO_2CO_3. These are the starting materials for all uranyl salts. Alternatively the oxides of uranium may be dissolved in HNO_3 to give uranium nitrate, $UO_2(NO_3)_2$. This on treatment with H_2SO_4 gives $UO_2(SO_4)$.

Uranium hexafluoride, UF_6: It is obtained as white crystals which sublimes at 57°C, by the action of excess of F_2 on heated metal. UF_6 is the most important halide of uranium. Mixed with UF_4 it is obtained by the action of F_2 on UCl_5. UF_4 being insoluble can be easily separated :

$$2UCl_5 + 5F_2 = UF_6 + UF_4 + 5Cl_2$$

It has been used for the separation of U^{235} and U^{238} in the vapour condition because of the difference in molecular velocities of $U^{235}F_6$ and $U^{238}F_6$ in a gaseous diffusion apparatus.

Yellow oxide of uranium, $Na_2U_2O_7.6H_2O$: When pitchblende is roasted with Na_2CO_3 and the melt is extracted with H_2SO_4 it gives $UO_2(SO_4)$ in solution. On adding alkali, such as NaOH solution, the precipitate obtained is

called uranium yellow (sodium uranate having the composition $Na_2U_2O_7.6H_2O$). It is used for painting porcelain and manufacture of fluorescent glasses.

Uranous oxide, UO_2 : When U_3O_8 is strongly heated in hydrogen the black dioxide UO_2 containing U^{+4} is obtained. UO_2 is soluble in concentrated acid giving the green solution containing UO^{+2} ion. UO^{+2} ion is also formed by reduction of UO_2^{-2} ion with zinc amalgam or Sn + HCl. UO^{+2} ion can be titrated with $KMnO_4$ solution for the quantitative determination of uranium.

Uranium tetrahalides : UCl_4 is obtained as a green crystals when UO_2 or U_3O_8 mixed with carbon is heated with Cl_2. It is soluble in water, alcohol and benzene. It is an intermediate in the preparation of uranium metal. UF_4 is obtained by the reaction of UCl_5 with F_2 or by adding a soluble fluoride to an uranus salt solution :

$$2UCl_5 + 5F_2 = UF_6 + UF_4 + 5Cl_2$$

UF_4 is insoluble in water.

Zinc and Magnesium uranyl acetate : These are double acetates of zinc acetate or magnesium acetate with uranyl acetate and is made by mixing the two in acetic acid solution. The yellow solution produces a yellow precipitate with Na^+ ion and is used for its identification.

Uses : Uranium is a strategic metal and is of great importance in the production of nuclear power. Apart from the industrial applications of the uranium compounds, it is used for the production of plutonium and other transuranim elements. The isotope U^{235} undergoes nuclear fission reaction with neutron whereas U^{238} undergoes neutron capture giving the transuranim elements.

Plutonium

Plutonium (element 94) is a strategic metal and an important member of the transuranium elements. Trace amounts of neptunium, Np, and plutonium, Pu, occur in nature in uranium minerals due to the natural radioactivity of uranium isotope, 235.

Both Np^{239} and Pu^{239} are found in the uranium fuel of the nuclear reactor. Pu^{239} is formed by the nuclear reaction.

$$_{92}U^{238}\ (n, \gamma)\ _{92}U^{239} \xrightarrow{\beta} {}_{93}Np^{239} \xrightarrow{\beta} {}_{94}Pu^{239}$$

Isolation of Pu : The separation of Pu from the reactor fuel elements is a difficult task because of the recovery operations for the starting material (uranium) and hazards involved in handling of highly radioactive fission products and high toxicity of Pu itself. The uranium fuel element from the nuclear reactor is dissolved in HNO_3 and the solution containing uranyl nitrate, $UO_2(NO_3)_2$. and Pu^{+4} is subjected to solvent extraction or precipitation or ion-exchange separation to isolate Pu from the fission products and uranium.

Metallic Pu : Metallic Pu is prepared by the same procedure as uranium. Reduction of PuF_6 with an alkali metal or Ba gives Pu metal at 1200°C. PuF_6 is a volatile solid and is less stable than UF_6.

Compounds of Pu : Plutonium forms a number of compounds with variable oxidation states of +2, +4 and +6. Thus oxides, halides, oxyhalides, nitrates, etc. of Pu have been made. PuO_3, $PuCl_2$, PuF_2, PuF_4, PuF_6, $Pu(NO_3)_4$ etc. are some examples. PuO_2^{+2} ion is less stable than uranyl, UO_2^{+2}, ion.

QUESTIONS AND PROBLEMS

1. Describe the preparation and uses of uranium tetrafluoride.
2. Write a short note on the chemistry of uranium.
3. Discuss the similarity of the chemistry of radium with that of other alkaline earth metals. How is radium extracted from pitchblende ?
4. Describe with a flow-sheet the extraction of thorium from monazite. Discuss the oxidation states of thorium.
5. Why is uranium so important in this age ? Describe a method for the extraction of uranium metal from pitchblende.
6. Write a short note on the uranyl ompounds. What is the use of zinc uranyl acetate?
7. Discuss the oxidation states of Ra, Th, U, Np and Pu with respect to their electronic configurations.

8. Describe the preparation, properties and uses of uranium tetrafluoride.
9. Prove that half-life of radium could be calculated if the disintegration rate of radium is known. How the half-life is related to the average life.

SOME MODEL QUESTIONS AND PROBLEMS

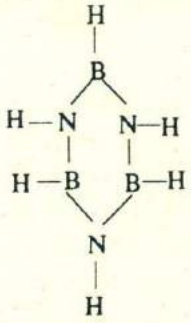
1. What are the maximum number of electrons in the following energy levels ?
   5d- 3f- 2s- 6f- lp- 4p-
2. 6.02×10^{23} molecules of oxygen weigh 32 g., calculate the wight of one atom of oxygen.
3. What element can produce a species having no electron at all. Give its various names and symbols.
4. The value of Rydberg constant is R = 190, 500 cm^{-1}. Calculate the wavelength of the second line (H_β) in the visible region of the hydrogen spectrum.
5. Show diagrammatically that electrons are small negatively charged particles.
6. What is the difference in the nuclear structure of the two isotopes of the same element ?
7. How would you prove that matter consists of atoms ?
8. Helium consists of two istopes having mass number 3 and 4. Indicate the atomic number, the number of protons, the number of neutrons and the nuclear charge for each of the isotopes.
9. Explain the presence of a large number of lines in the hydrogen spectrum although hydrogen contains only one electron.
10. How many valence electrons have carbon, silicon, phosphorus, hydrogen ? Write the electron configurations for neutral atom of each element.
11. Give the values of all four quantum numbers for each of the ten electrons of the neon atom.
12. Distinguish between the four general types of elements, and explain how their chemical properties differ.
13. How does the electron structure of atoms of metals differ from that of atoms of non-metals ?
14. From their positions in the Periodic Table predict the chemical properties of astatine and francium.
15. From the relative position of radium in the Periodic Table predict the solubilities of its hydroxide and sulphate.

16. Explain the small differences in the sizes of the atoms of Cu, Ag and Au and their ions as compared with the large differences in the sizes of the alkali metal atoms and their ions.
17. The atomic number of the mythical element centaurium (Ct) is 117. (a) Indicate the likely atomic structure. (b) In which family will it be found ?
18. Give brief explanations of the following :—
    (a) LCAO, (b) Orbit and Orbital, (c) Radius-Ratio effect in ionic crystals, (g) Fajan's Rule.
19. Arrange the following bonds in order of their ability to distort negative ions :—
    Al^{+3}, Cs^{+}, Cr^{+3}, Cr^{+6}, Rb^{+}, Sr^{+2}, Xe.
20. Arrange the following bonds in order of increasing ionic character :
    Be—O, C—O, N—O, O—O, Si—O, Se—O. Indicate the Bond Order for each.
21. Predict the configuration of each of the following ions or molecules :
    (a) BH_4^-, (b) NH_4^+, (c) Br_3^-, (d) D_2Se, (e) $Co(SCN)_6^{-3}$, (f) $SiCl_4$, (g) $Cr(NH_3)_6^{+3}$ and (h) SbH_3.
22. Write Lewis structure for each of the following ions and discuss about their properties :
    PO_4^{-3}, PO_3^{-3}, ClO_2^-, ClO_3^-, SO_3^{-2}, SeO_4^{-2} and IO_4^-,
23. The molecular formula of some substances are given below. Discuss the types and nature of the chemical bonds between the respective atoms of the molecules. How the properties of the molecules are influenced by the bonds in these molecules ?
    H_2O, NH_3, H_2SO_4, MgO, $AlCl_3$, $Co(NH_3)_6Cl_3$, NH_4Cl, CO_2, SO_3, NO_2, SF_6, KCl, HNO_3, HF, H_2PO_3, H_3PO_2, H_2O_2.
24. "HCl is a covalent compound but ionizes in water to produce H_3O^+ ion." Explain.
25. "Ionic compounds dissolve in polar liquid and covalent compounds dissolve in non-polar liquids." Is the above statement always true ? Discuss.
26. Why is sodium chloride a better conductor of electricity in a molten condition than in the solid state ?
27. What is the difference between a polar and a non-polar compound ?
28. Are all covalent compounds non-polar ? Explain.
29. Why would you expect ionic compounds normally to have higher melting points than covalent compounds ?
30. Why should you expect the melting point of NaCl to be much higher than that of $AlCl_3$?

31. Which compound should be more ionic, AlF_3 or $AlCl_3$? Give reasons for your answer.
32. Why do some elements have more than one ionization potential ?
33. How can the electronegativities of the elements be used to predict what kind of bond will be formed when two elements combine ? Illustrate your explanation with specific examples.
34. In general, the first ionization energies (energies required to remove one electron from the neutral atom I_1 increase as we go across the second period (see below). Why ? However, boron and oxygen exhibit anomalous behaviour ; their ionization energies are lower than expected. Examine the electronic configuration of these elements and suggest why :

	Li	Be	B	C	N	O	F	Ne
I_1(ev)=	5.4	9.3	8.3	11.3	14.5	13.6	17.6	21.6

35. Discuss the nature of bonding in the molecules H_2S, PH_3, SiH_4 and P_2H_6., Be specific about bond angles, number of σ and π bonds, lone pairs, type of hybridization and cores and bond orders.
36. The molecule CO_2 is linear with the carbon atom between the oxygens. Discuss with pictures the probable bonding in this molecule. Draw a classical line structure consistent with your model.
37. Suggest on the basis of orbital theory two possible geometric structures for the molecule P_4. The four phosphorus atoms are equivalent.
38. The CO_3^{-2} ion is a planar one with the carbon atom in the centre of a triangle formed by the oxygens. Discuss the bonding in this molecules.
39. The molecule borazole, $B_2N_3H_6$, has the framework :



Discuss the bonding in this molecule.

40. Discuss reasons why the compound OF_6 has never been observed while SF_6, in principle a member of the same family of compounds, is known.

41. What forces hold polar molecules together ? Explain their source and operation.
42. How is the polarity of a bond related to the electronegativities of the atoms which are held together by the bond ?
43. Account for the shape of the water molecule.
44. Explain the occurrence of the hydrogen bond in water and hydrogen fluoride.
45. Why would you expect H_2O to be more polar than H_2S ?
46. Discuss the properties of water in relation to the hydrogen bond.
47. Explain the wide difference between the boiling points of H_2S, and H_2O.
48. State the types of bonds which would be expected in crystals of (a) krypton, (b) ice, (c) carbon tetrachloride, (d) diamond, (e) copper, (f) magnesium nitrate, (g) potassium chloride and (h) hydrogen fluoride.
49. Explain why the boiling point of the inert gases increase with increase in atomic size.
50. KF reacts with HF to form a solid of formula, KHF_2. Discuss the probable geometry and bonding in the HF_2^- ion.
51. The density of liquid water is considerably greater than that of solid water i.e. ice floats on water. Suggest an explanation in terms of hydrogen bonding and structure.
52. Discuss briefly the significant features in the properties and structures of the following pairs :—

    (a) H_2O and H_2S (b) AgF and AgCl
    (c) NCl_5 and PCl_5 (d) SF_6 and UF_6
    (e) CO_2 and SiO_2 (f) $SnCl_4$ and $SiCl_4$
    (g) $AlCl_3$ and BCl_3 (h) Li_2CO_3 and $MgCO_3$

53. Explain the following observations :—
    (a) Silver fluoride is colourless and soluble in water whereas silver iodide is coloured and insoluble.
    (b) Water burns in fluorine, but not in oxygen.
    (c) Hydrazine is suitable for rocket fuel.
    (d) NCl_5 does not exist, whereas PCl_5 does.
    (e) Zirconium and hafnium have almost identical properties.
    (f) Liquid HCl does not conduct electricity whereas an aqueous solution of HCl is a good conductor.
    (g) The transition metal ions are generally coloured.
    (h) $Co(NH_3)_6 Cl_3$ is more stable than $Co(NH_3)_6Cl_2$.

54. The outermost orbitals of (i) He, (ii) alkaline earth metals, (iii) the transition metals, (iv) Zn, Cd and Hg. (v) the lanthanides and (ii) the actinides all have s^2 electrons in the outermost energy levels. Explain why their properties are vastly different.

55. Give reasons for the following :—

(a) Carbon, a non-metal, is a good conductor of electricity and is used as electrodes.

(b) NF_3 is more stable than PCl_3.

(c) CuI_2 is unstable, $CuCl_2$ is stable.

(d) AgF is colourless and soluble in water, AgI is coloured and insoluble.

(e) CO_2 is a gas at ordinary temperature, SiO_2 is a solid of high melting point.

(f) Cu is red, Ag is while and Au is yellow.

(g) HNO_3 is a stronger acid than H_3PO_4 but H_3PO_4 has a higher boiling point than HNO_3.

56. Mention the strengths of the following acids and arrange them in the increasing order of the strengths :

HClO H_2SO_4 HNO_3 H_4SiO_4 H_3PO_3 $HClO_4$

57. A pure ionic compound was placed in a tightly sealed flask and nearly all the air removed. After several week the gaseous phase in the flask was examined and an appreciable amount of helium found. Interpret this finding.

58. Write balanced nuclear reactions for the decay of :—

Rn^{222} by α-emission.

Cd^{115} by β- emission,

Br^{75} by position emission.

Zn^{62} by K-capture.

59. Compare alpha, beta and gamma rays in terms of mass, charge and penetrating power.

60. Explain the conditions that exist in a radioactive equilibrium.

61. Explain why rates of radioactive disintegrations are given in terms of half-life periods.

62. An isotope of thorium, Th^{232}, undergoes a series of disintegration to form a stable isotope of lead, Pb^{208}, as an end product. How many alpha and beta particles are emitted in the total decay of one atom ?

63. The half-life of Fr^{221} is 4.8 min. Starting with 1 mg of the isotope, how much would remain after 30 min ?

64. Explain how the most abundant isotope of uranium, U^{238}, can be converted into plutonium.

65. It is said that plutonium—239 with a half-life of 24,000 years, is found in nature in minute traces. Account for this occurrence.
66. Explain the difference between nuclear fission and nuclear fusion.
67. Practically all artificial isotopes used in tracer investigation are beta emitters. Why should this be true ?
68. The half-life of sulphur 37 (beta emitter) is 5 min. If you were given 80 g. of the nuclide at 9 A. M. on a Monday morning, how much of it would you have at 10 A. M. the same morning ?
69. Write equations to represent the following nuclear transformation :—
(a) Be^{9} (α, n) ; (b) K^{39} (p, α), (c) Na^{23} (d, α), (d) Bi^{200} (d, n).
70. Suppose we have a few grams of $RaSO_4$ which is, of course, radioactive . Is the half-life of this material the same as the half-life of (radioactive) RaO ? Why, or why not ?
71. Prove that the Average life of a redioelement is equal to 1.34 x half life time.
72. Calculate the time in which the radioactivity of a sample of thorium reduces to 90% of its activity. Given $t_{\frac{1}{2}}$ of Th = 1.4×10^{10} years.
73. Calculate the number of α- and β-particles emitted by $_{92}U^{238}$ when it changes to $_{82}Pb^{206}$.
74. How long it will take for 25% of the sample of Ac^{227} to disintegrate. Half-life of Ac^{227} is 22 years.
75. A piece of wood contained C^{14}/C^{12} ratio = 0.7 of that in a living plant. Calculate the age of the wood "t". Half-life of C^{14} = 5760 year. Use the equation

$$t = \frac{2.303\ t_{1/2}}{0.693} \log \left[\frac{C^{14}/C^{12} \text{ ratio in the fresh wood}}{C^{14}/C^{12} \text{ ratio in the old piece of wood}} \right]$$

76. The ratio of C^{14}/C^{12} in a piece of wood was found to be 13% of the atmosphere. Calculate the age of wood. Half life of C^{14} = 5700 year.
77. Complete the equation.
(a) $_{92}U^{236} \longrightarrow {}_{90}Th^{234} + ?$
(b) $_{11}Na^{24} \longrightarrow {}_{12}Mg^{24} + ?$
(c) $_{6}C^{12} + {}_{1}H^{1} \longrightarrow$
(d) $_{17}C^{135} + {}_{0}n^{1} \longrightarrow$

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